

Carnegie Mellon University

CARNEGIE INSTITUTE OF TECHNOLOGY

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF Doctor of Philosophy

TITLE Friction Control by Adsorption of Polymer Brush Nanoparticles

PRESENTED BY John Riley

ACCEPTED BY THE DEPARTMENT OF

Chemical Engineering

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Submitted in partial fulfillment of the requirements for
the degree of
Doctor of Philosophy
in
Chemical Engineering

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April 2016

Acknowledgements

First and foremost, I'd like to thank my advisor, Bob Tilton, for overseeing my PhD research. He encouraged my best efforts in the laboratory, pushed me to think deeply and cynically at my research, and afforded me every opportunity to present and publish my work. Having inspired me to become a professor one day, I can only hope to emulate his thoughtful, dedicated, and tolerant approach to teaching, research, and advising. I am fortunate to name him as a professional mentor and personal friend.

I sincerely thank my committee members Steve Garoff, Andy Gellman, and Jim Schneider for their input during the proposal exam and thesis defense. Professor Schneider has been particularly helpful in discussing AFM instrumentation and experiments over the course of my PhD research. I've also enjoyed my close interaction with Professor Garoff, and the scientific discussions spurred on by members of his research group have made me appreciate the complementary mindsets held by physicists and engineers.

This research, and my growth as scientist, were enriched by the many collaborators that I've had the pleasure of working with. Special thanks to Professor Krzysztof Matyjaszewski and collaborators in his polymer synthesis research group at CMU. I was afforded the unique opportunity to work closely with the world-leading experts in controlled radical polymerization, and both my PhD research and future research efforts benefitted immensely from our interactions. Thanks to Dr. Benjamin Chi-Ming Hui, Melissa Lamson, and Yi

Wang for providing well-synthesized materials. Importantly, I'd like to thank Dr. Sangwoo Park for teaching me the nuts-and-bolts of running ATRP reactions and contributing immensely to my polymer chemistry skillset and understanding of ATRP.

I would like to thank Professor Per Claesson, Professor Esben Thormann, and Dr. Xiaoyan Liu at the KTH Royal Institute of Technology in Stockholm, Sweden for welcoming me to their lab during the first year and teaching me how to perform colloidal probe force and friction measurements. Special thanks to Junxue An, whom I had the pleasure of working with both at KTH and during her time as a visiting PhD student at CMU. Junxue and I worked in tandem to study the interactions between SDS and PDMAEMA-grafted nanoparticles and we published a very nice paper together.

I would also like to acknowledge the undergraduate and MS students that I had the opportunity to work with and mentor during my PhD work: Jordan Green (UG), Jackie Budz (UG), Ryan Trottier (UG), Zack Zhong (MS), Yihan Wang (MS), Owaiz Ebrahim (MS), Bhagyashree Lele (MS CPS), and Wenjie Wu (MS). Most notable contributions to the work in this dissertation were made by: Ryan Trottier (Hoffmeister effects on star PEO), Owaiz Ebrahim (star PEO/linear PEO competitive adsorption), Bhagyashree Lele (stability of latex with adsorbed stars and BGNPs) and Wenjie Wu (block star cloud point measurements).

A number of professors at CMU merit acknowledgment. Thanks to Annette Jacobson, Susana Steppan, and Rose Frollini for managing the CPS laboratory, where many of the experiments in this dissertation were performed.

Also, thanks to Annette, Susana, and Rose for actively organizing outreach opportunities that were extremely rewarding to participate in. Professor Paul Sides provided guidance on ZetaSpin streaming potential measurements, and I'm thankful for our many scientific discussions both at CMU and on the golf course.

I am also thankful to many others in the Department of Chemical Engineering for creating a stimulating environment that was both a beautiful place to perform graduate studies and research, and also a place that felt like home. Special thanks to all the members of the Tilton group who I've had the honor to work with closely in the lab and in group meetings. Thanks to Dr. Adam Canady and Dr. Stacy Pustulka-Wirth, the senior group members who mentored me in my first year and helped get me going on early laboratory work. Thanks to the many likeable coworkers that I've worked and studied alongside, particularly those in the BIO and CFE labs. I would especially like to thank Ben Yezer, Steve Spagnol, Pat Boyer, and John Goldman, for being the best group of friends to share a graduate school experience with.

I must express the most heartfelt thanks to my girlfriend and family. To Rachael Troianos, I am so fortunate to have met you during the grind of my fourth year. You have brought me a special kind of happiness, and the next phase of life is all the more bright with you by my side. To my brother Joe, our "sibling rivalry" has pushed me to be better professionally and personally, and I cannot express my gratitude for the sterling example you set for me to ascribe towards. To my sister Erin, I am thankful for the year-and-a-half we got to spend together living in Pittsburgh and all the support you have provided. Finally, to my parents

Patrick and Angela. This dissertation, and much of what I have accomplished along the way, was only made possible by the values and passions that I have learned from you both. Thank you for the loving, supportive upbringing you continue to provide me with, day-in and day-out.

Sources of support

This material is based on work supported by the National Science Foundation under grant CBET-1133175 and in part by the Carnegie Mellon University Department of Chemical Engineering, a Carnegie Institute of Technology John and Claire Bertucci Graduate Fellowship, and an Eastman Chemical Company Summer Graduate Fellowship.

Abstract

This dissertation investigates the adsorption of polymer brush nanoparticles (BNPs) at the solid/liquid interface and interactions between BNP coated surfaces undergoing compression and sliding. BNPs are a class of materials defined by their nanoscale core and surrounding spherical brush layer of polymer arms. BNPs developed in this dissertation are created using atom transfer radical polymerization (ATRP) and include polymer grafted silica nanoparticles, star polymers with a corona of arms crosslinked with a dense hydrophobic core, and star polymers with arms emanating from a multi-functional molecular core. Assemblies of BNPs at the solid liquid interface can attain relatively low or high surface coverages which, when paired with a responsive polymer brush nanoparticle, enables additional control of interactions between BNP adsorbed layers via tunable surface coverage and particle-surface bridging forces. Strategies for controlling the adsorption and packing of these BNPs are presented, and surface forces between BNP coated surfaces are measured to assess each type of BNP's ability to control friction and adhesion between silica surfaces. Direct adsorption strategies which produce single BNP type adsorbed layers, and sequential adsorption strategies which form surfactant/BNP, polyelectrolyte/BNP, and BNP/BNP mixed layers are employed to generate a full suite of surface coatings with uniquely-engineered structural, frictional, and adhesive characteristics.

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1. Introduction

This dissertation presents polymer brush nanoparticles as a versatile class of surface-active materials capable of adsorbing at the solid/liquid interface and, with the appropriate choice of polymer brush nanoparticle structure and properties, inducing stimuli-responsive adhesion and friction between surfaces in intimate contact or undergoing relative sliding motion. **Figure 1.1** provides a schematic overview of polymer brush nanoparticle-mediated surface forces.

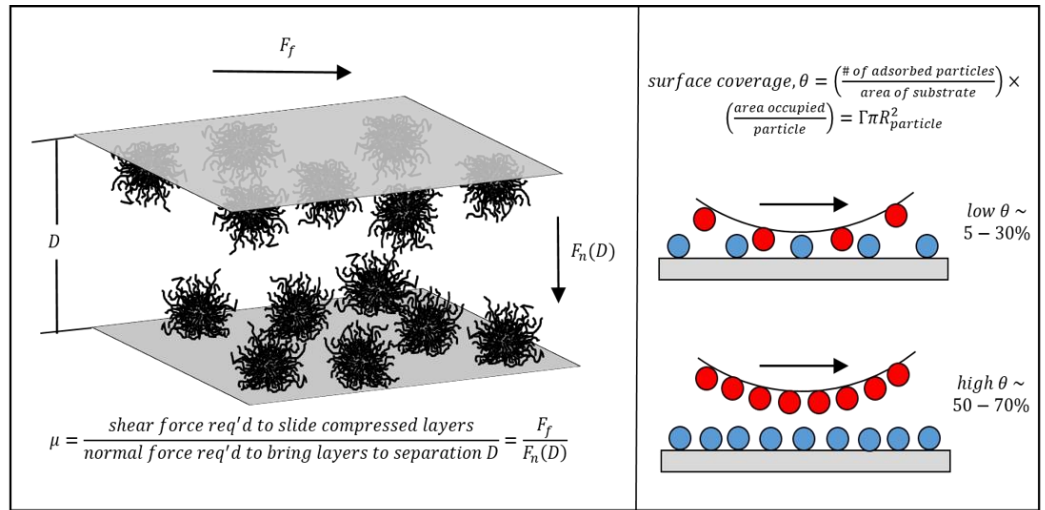


Figure 1.1. *Summary of key physics.* Polymer brush nanoparticles adsorb to surfaces to form laterally heterogeneous layers, and the coefficient of friction will be determined from measured normal and friction forces between the nanoparticle-decorated, solvated surfaces. Surface coverage plays a vital role in the effective interactions between brush nanoparticle adsorbed layers. At low coverage the average interparticle spacing is greater than the particle diameter, enabling interdigitation between particles on opposing surfaces and the formation of attractive particle bridges which act to resist the onset of sliding motion. Once interdigitated, the particles are obstructed and must either “rise and fall” or plow through neighboring particles, forcing their dislodgement from the surface. High coverage surfaces mimic homogeneous planar brushes and impart strong repulsions that result in a fluid interfacial region capable of supporting low-friction sliding. Inclusion of stimuli-responsive polymers into the brush nanoparticles allows coverage and bridging to be modulated by triggered changes in the swelling state of surface-adsorbed brushes.

1.1 Motivation

Many processes in nature and technology are enabled or restricted by friction between interacting components within a system. During the rubbing of bones in mammalian joints, contact is mediated by a combination of soft articular cartilage and surface active biopolymers in the synovial fluid¹⁻³. The composition and structure of this lubricant system determines the amount of pressure which the joint can support (~ 10 MPa), the ease with which the joint can move, and the rate at which the joint is worn. Oil-based lubricants contain additives⁴, often surface-active fatty acids and viscosity-enhancing polymers, and act to reduce contact, promote sliding motion, and mitigate temperature increases between surfaces under extremely high loads (~ 1 -50 GPa) such as automotive gears and bearings or machine finishing/cutting tools. Micro-electro-mechanical systems (MEMS) devices have many promising applications, for example lab-on-a-chip diagnostics, actuation and sensing, and display technologies, but are severely limited by strong adhesive forces^{5,6} (e.g. surface tension, capillary, electrostatic, and van der Waals) which bring the structured surfaces into contact and drastically increase friction and wear upon motion. Robust surface treatment schemes which inhibit contact during production and use of the devices is required before large-scale realization of MEMS technology is possible. Conversely, friction is desired to some degree in the food industry^{7,8}, as it contributes to the oral texture and feel of a food product. Fat and water content sometimes must be modified to enhance or reduce friction and satisfy aesthetic consumer demands. In the field of colloidal suspension and granular rheology, recent studies have proposed that frictional contacts between particles in dense-suspensions cause strong shear-thickening

rheological behavior⁹. Control over frictional interactions in these suspensions could critically determine macroscopic flow properties, especially in the limit of high shear rates. Thus, research into novel friction control schemes with tunable, responsive behavior may provide technological benefits across a broad range of processes which cover length scales from the nano- to macro-scale.

Polymer brushes are an important class of material structures used for interfacial engineering and consist of multiple polymer chains anchored by one end to a surface with the free ends extending into solution, characterized by a stretched conformation that depends on the solvent quality and the lateral grafting density of chains. Unique features of polymer brushes, including their strong swelling and resistance to compression under good solvent conditions¹⁰ and the presentation of a large number of chemical functional groups over a small surface area, lend themselves to a variety of technological applications such as colloidal stabilization,^{11,12} emulsification,^{13–15} boundary lubrication,^{16–18} and nanoparticle/protein immobilization.^{19–21}

A simple and commonly employed method for forming polymer brushes is to adsorb block copolymers consisting of adsorbing “anchor” blocks and non-adsorbing “buoy” blocks from solution.^{22–24} Nevertheless, attainment of high grafting densities can be limited if the nominal buoy block has affinity for the surface,²⁵ and kinetic limitations that hinder adsorption as the surface approaches saturation often prevent adsorbing block copolymers from achieving the very high grafting densities that produce the desired strong chain stretching. Similar kinetic constraints limit grafting densities and chain stretching that can be achieved by

covalently grafting end-functionalized polymers to a surface.^{26–28} To remedy problems of low chain grafting density, and sometimes weak chain attachment, the “grafting from” method of brush formation was developed, whereby polymer chains are grown from surface-bound initiators.^{29,30} In this fashion, covalently-attached high grafting density brushes with well controlled properties are formed. This method has obvious advantages relative to simple adsorption based schemes, but it does lack their flexibility for application in many different systems. For example, a need to avoid harsh reaction conditions or the absence of suitable surface chemical functionalities may preclude use of the grafting from method.

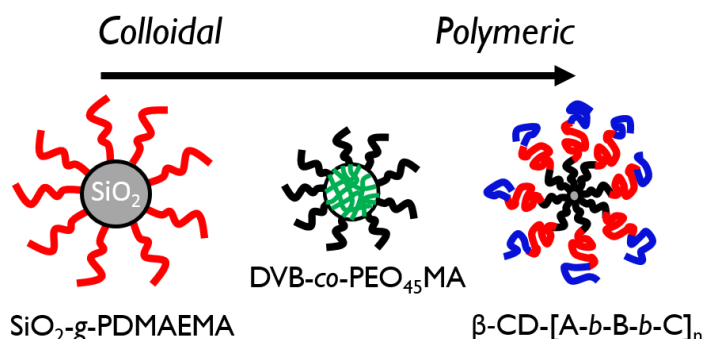


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In an effort to combine the advantages of high chain density and stretching with the flexibility of adsorption-based strategies, we consider adsorption of brush nanoparticles (BNPs) to the surface of interest. BNPs consist of a nanoscale core that has been functionalized with a dense corona of polymer arms. Examples of BNPs include multi-arm star polymers with crosslinked cores as well as

polymeric or inorganic nanoparticles with polymers grafted from their surfaces^{31–35}. The core/corona structure of a BNP is similar to a block copolymer micelle, except the chains comprising the corona are covalently attached to the core and disassembly is not possible³⁶. Example nanostructures developed in this dissertation are provided in **Figure 1.2**. BNPs can be adsorbed from suspension to an interface to form a “pseudo-brush” or “patchy brush” layer. A high-grafting density brush on the nanoparticles will ensure that a large number of chains contact the surface to promote strong attachment and that a large number of highly stretched chains extend away from the surface into solution.

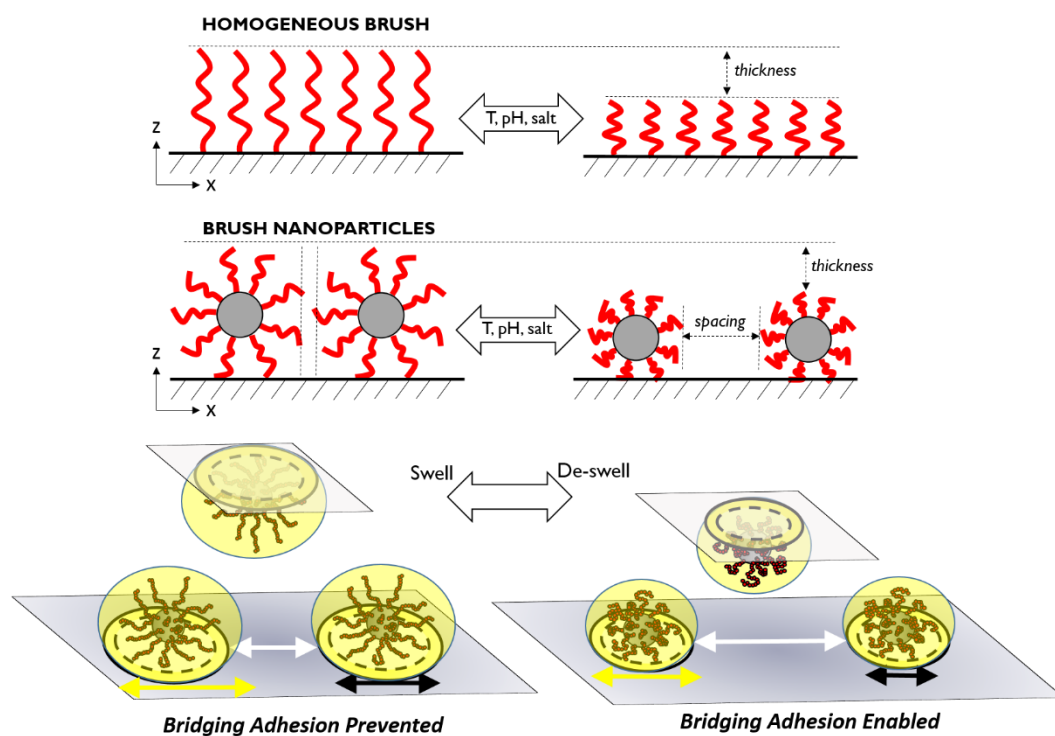


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An adsorbed BNP layer would be discontinuous, with gaps between individual BNPs. Lateral repulsions among adsorbing BNPs will limit attainable surface coverage. Adsorption of uncharged BNPs is limited by steric interactions, and poly(ethylene oxide) star polymers have been used to form high-coverage surface coatings.³⁷ Adsorption of polyelectrolyte BNPs to oppositely charged surfaces is controlled by the balance of electrostatic attraction to the surface and lateral electrostatic and/or electrosteric repulsions. Patchy adsorbed layers will have significantly different interactions than well-defined, high-grafting density brush layers³⁸; however, this provides an extra degree of freedom toward modulating layer properties and interaction forces as depicted schematically in **Figure 1.3**. Planar brushes are limited to swelling changes predominantly in the direction perpendicular to the surface, while adsorbed BNPs with responsive polymer coronas exhibit swelling both parallel and perpendicular to the surface. An example where this is beneficial is in adhesion and friction control applications. Planar brushes can be switched between adhesive and repulsive owing to changes in pH or temperature³⁹, but the strength of the adhesions are limited to polymer-polymer attractions, and for planar brushes, segment-segment attractions coincide with brush collapse which minimizes the effective surface area of adhesive contacts that can be made. Decreased friction upon planar brush collapse has been observed for a pH and thermoresponsive brush, owing to the collapse and decreased roughness of the surfaces⁴⁰. In a patchy BNP layer, both polymer-polymer attractions and polymer-surface bridging can contribute to the overall adhesion strength and frictional interactions. With the goal of controlling

friction and generating surfaces with tunable interactions, BNPs can utilize triggered bridging interactions in ways that are not accessible to planar brushes. If the BNPs are functionalized with a stimuli-responsive polymer, then swelling changes can be used to block or allow bridging phenomena. This offers a potentially exciting and useful route for tunable adhesion and friction properties manifested by adsorbed BNP layers.

1.2 Dissertation objectives

The overarching goal of this dissertation is to develop friction and adhesion control strategies based on adsorption of novel polymer brush nanoparticles. This objective will be met using a “bottom-up” approach that involves: 1) rational design of polymeric nanoparticles with controlled structure and chemistry, 2) characterization of the materials based on their colloidal and polymeric physical chemistry, 3) brush nanoparticle adsorption onto solid substrates and structural characterization of the adsorbed layers, and 4) measuring interaction forces in response to compression and shear of brush nanoparticle adsorbed layers.

This dissertation will attempt to provide a comprehensive assessment of the adsorption properties of non-ionic and polyelectrolyte-based brush nanoparticles. To our knowledge, there are no studies that systematically investigate the adsorption of these types of nanostructured polymeric materials at solid/liquid interfaces. In addition, the dissertation will address a fundamental gap in the literature pertaining to interactions, including lateral friction forces, between patchy polymer brush-like layers. Finally, this dissertation will utilize a

number of traditional and non-traditional adsorption processing methods to investigate non-equilibrium and multi-component adsorbed layer structures and their resulting surface forces. This will include the study of BNP adsorption hysteresis, complexation of surfactant to BNPs, and multi-layering strategies with secondary macromolecular components.

1.3 Outline of dissertation

The dissertation is organized into nine chapters, and these can be grouped together into sections based on general approach and research question addressed. The summary below intends to provide context and format for the logical flow of the dissertation:

Chapter 1 presents a broad introduction, including an overview of the thesis problem and the key related physics. Chapter 1 provides brief literature reviews for each of the major topical areas relevant to the thesis problem: *tribology, polymer adsorption, and colloidal forces*.

Chapter 2 includes a description of all experimental techniques and materials utilized in the course of this dissertation. The major body chapters will refer back to Chapter 2 for detailed experimental procedures, avoiding repetitious “Materials and Methods” sections throughout.

Chapters 3, 4, and 5 provide detailed investigations of the formation of polymer brush nanoparticle adsorbed layers and the surface forces that arise from these layers. This section of three chapters is comprehensive in describing *single component* polymer brush nanoparticle layers and interrogating fundamental

relationships between solution conditions, particle properties, layer conformation, and surface forces.

Chapters 6 and 7 present studies of *multi-component* adsorbed layers, including mixed layers of polymer brush nanoparticles with small molecule surfactants, linear polyelectrolytes, and other brush-like macromolecules. This section provides strategies for circumventing limitations of single-component adsorbed layers by sequential and co-adsorption techniques. The strategies developed here are relevant toward the inclusion of polymer brush nanoparticles in common complex fluid formulations and also assembly of thick, conformal lubricant coatings.

Chapter 8 presents the full development and evaluation of new, rationally designed polymeric lubricants. *Multi-component star polymers* are engineered as a direct result of the research findings described in the preceding chapters. The novel star polymers display excellent lubricant properties and switchable friction and adhesion. The inclusion of novel polymer synthesis, polymer and colloidal characterization, adsorption properties, and surface forces allow this Chapter to serve as a true microcosm of the larger dissertation work and a suitable closing body chapter.

Chapter 9 concludes the dissertation by providing not only a summary of major findings and future directions for the research project, but also offering perspectives on the diverse polymer brush nanoparticle-based strategies developed throughout the dissertation.

It is important to note that this dissertation, read in full, includes all research findings and detailed discussions of these findings. However, the dissertation is written such that Chapter 1 and Chapter 9 can be treated as a truncated, high-level discussion of the full thesis problem. Chapter 8 can be read in addition to capture the full research philosophy employed throughout the dissertation in a single chapter.

1.4 Background

1.4.1 Polymers at solid/liquid interfaces

Polymer adsorption to an interface is driven by a balance between enthalpic interactions that drive adsorption and entropic losses that resist confinement. Enthalpic interactions that influence adsorption include attractive polymer-surface interactions and the relative strengths of solvent-polymer and solvent-surface interaction that arise when a monomer adsorbs at an interface and displaces structured polymer-solvent and solvent-surface molecular contact. Favorable segment-surface interactions are $\sim k_b T$ per segment adsorbed, and polymers consisting of a large number of segments can attain very large adsorption energies by multi-segmental contact with the surface. The anchoring of monomers at the surface perturbs the equilibrium three-dimensional structure of the bulk, solvated polymer, and this results in a penalty to adsorption via a reduction in the configurational entropy of the system. The balance of these forces result in homopolymer adsorbed layers like the one depicted in **Figure 1.4**. Linear homopolymers will form loops and tails in an attempt to minimize entropy losses, but form favorable train contacts with the surface to realize enthalpic energy

benefits. The loop-tail-train structure of linear polymers highlights how the balance of enthalpic and entropic forces dictate the adsorbed layer structure of polymers at interfaces. Additional contributions, such as counterion release and electrostatics, play an important role for the adsorption of polyelectrolytes, but will not be discussed in detail here. The reader is referred to the literature^{41–43} and a comprehensive textbook⁴⁴ for further reading.

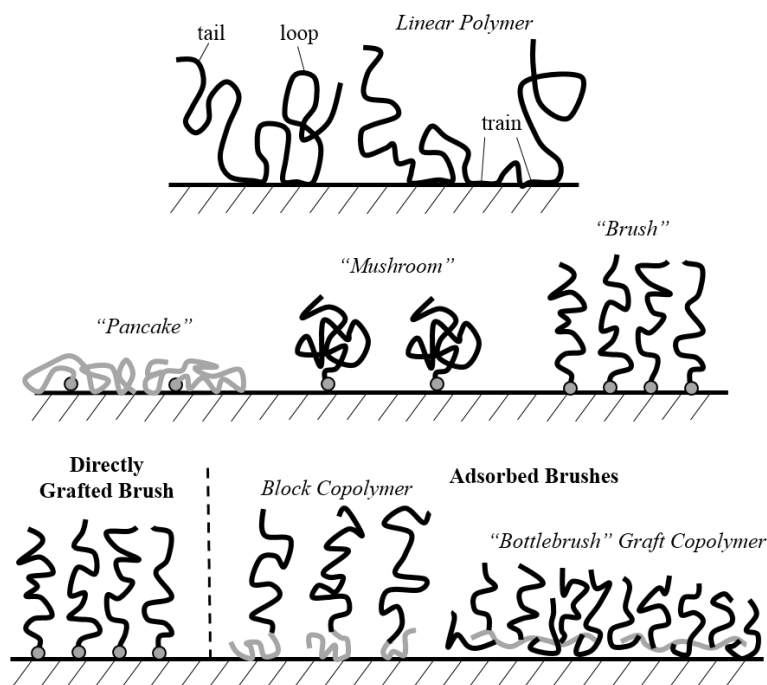


Figure 1.4. Structure of polymers adsorbed to a solid/liquid interface.

Other important interfacial polymeric layers and microstructures are depicted in **Figure 1.4**. Tethering a polymer chain to an interface can result in a variety of layer structures, which were first identified by de Gennes⁴⁵: a “pancake” layer when polymer-surface interaction is favorable, a “mushroom” layer when polymer-surface interaction is unfavorable and the grafted chains are sparsely populated on the surface, and a “brush” layer when the chain density is

increased and polymer-solvent interactions are more favorable than polymer-polymer interactions. Polymer brushes have garnered much attention in the literature^{46–48} and form one of the cornerstones of the research in this dissertation. Brush layers can be formed by direct grafting methods, adsorption of block copolymers, or adsorption of bottle-brush copolymers. The physics of grafted brushes are relatively well understood, and bottle-brush polymer adsorption has garnered significant attention from a number of groups^{49–51}. These layers have been discussed in more detail in the “Motivation” section presented earlier in the chapter.

Adsorption of polymer brush nanoparticles is again subject to the same balance of forces discussed above. A number of simulation studies have been performed to predict the types of adsorbed layer structures formed by polymer brush nanoparticles⁵², branched dendrimers^{53,54}, and star polymers^{55–57} at the solid/liquid interface. The phase behavior of adsorbed polymer brush nanoparticles and similar structures largely depends on the number of arms and length of each arm. As the number of arms increases the polymer corona becomes increasingly rigid due to intrabrush segment-segment repulsions, resulting in a particle conformation that is difficult to perturb. Thus, a number of segments will contact the surface but the particle will retain its three dimensional conformation and appear more or less as a weakly-perturbed droplet or colloidal particle. We suspect this is the situation for most of our densely grafted polymer brush nanoparticles. As the arm number decreases, the brush layer will be less

constrained and more capable of making intimate contact with the surface, effectively flattening the structure.

Importantly, the adsorption of polymer brush nanoparticles must be thought about as a synergy between colloidal deposition and polymer adsorption principles, as depicted in **Figure 1.5**. While the BNP may adsorb more or less as a sphere on the surface, the local contact and adsorption dynamics are governed by polymer-surface contacts and entropy/enthalpy balances discussed above.

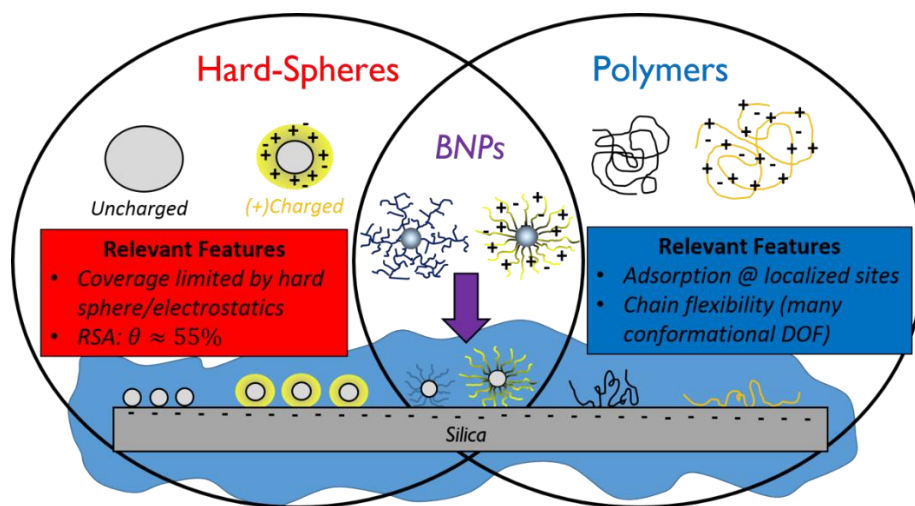


Figure 1.5. Hybrid colloidal/polymeric representation of brush nanoparticles and their assembly at the solid/liquid interface. Adsorption of the particles is governed locally by polymer-surface interactions⁴⁴. Brush nanoparticles with many arms will weakly deform at the surface⁵⁵ and their apparent shape is similar to that of a 3D colloid or nanoparticle.

1.4.2 Colloidal forces

The interactions between surfaces bearing adsorbed polymer layers are extremely complex, and relatively few established theories can accurately capture all features displayed in AFM or SFA measurements. This section briefly discusses the classical forces that are expected to play a role in the normal and

frictional forces arising from brush nanoparticle coated surfaces. Readers are referred to the excellent text by Isrealachvili⁵⁸ for a full discussion.

The starting point for almost all analysis of colloidal forces is DLVO theory of colloidal stability. Developed by Derjaguin, Landau, Verwey, and Overbeek in the 1940s, it is based on the assumption that the total force between colloidal particles is the sum of van der Waals and electrical double layer interactions. DLVO theory is most widely used to describe the stability of colloids in response to changes in salt concentration and valency, but is well known to fall short of providing a comprehensive description of interaction forces between real surfaces bearing structural or chemical complexity. The force between a sphere of radius R and a flat plate in DLVO theory is:

$$F_{DLVO}(D) = F_{DL} + F_{vdW} \\ = 64\pi\epsilon\epsilon_0\kappa R \left(\frac{k_B T}{e}\right)^2 \tanh^2\left(\frac{ze\psi_0}{4k_B T}\right) e^{-\kappa D} - \frac{AR}{6D^2} \quad (1.1)$$

Where the electrostatic contribution F_{DL} increases exponentially as the surface separation distance D is decreased. The decay length of the double-layer forces is characterized by the Debye parameter κ :

$$\kappa = \sum_i \left(\frac{\rho_{\infty,i} e^2 z_i^2}{\epsilon\epsilon_0 k_B T} \right)^{1/2} \quad (1.2)$$

The Debye length κ^{-1} depends on the bulk concentration ρ_{∞} and valency z of each ionic component in the intervening electrolyte reservoir. The pre-factor for the double-layer interaction force is a function of the particle radius, Debye length, and particle electric potential ψ_0 , which is related to the surface charge.

The van der Waals force F_{vdW} is longer range than F_{DL} and depends on the Hamaker constant A of the interacting surfaces across the medium and the particle size. The interplay between van der Waals and double layer forces can result in attractive, repulsive, or a mix of the two for a given set of solution conditions and particle and surface properties. Double layer forces will play an important role in the interactions between polyelectrolyte BNP coated surfaces, and always are present due to the strong surface charge of silica utilized as substrates throughout the dissertation.

Steric interactions between adsorbed polymer brush nanoparticles will also contribute to the net surface interactions. A first representation of a patchy BNP layer can be made by approximating each adsorbed particle as a “mushroom” on the surface. Mushrooms are grafted to the surface, but extend away in a spherical conformation characterized by their unperturbed radius of gyration R_g and do not overlap or interact with neighboring adsorbed particles. The total density of mushrooms is given by Γ . Most of the layers encountered in this dissertation are “patchy” in nature, and the isolated nature of the particles is reminiscent of mushroom-type polymer grafts. Upon compressing two layers of “mushrooms” to a separation D such that the mushrooms on opposing surfaces begin to overlap, the resulting force again displays an exponential force law:

$$F_{steric} \approx \frac{36\Gamma k_B T}{R_g} e^{-D/R_g} \quad (1.3)$$

Where the decay length of the repulsions are now characterized by the inverse radius of gyration of the chain, or in the case of BNPS, likely the thickness of the

brush on the particle. It is apparent here that the repulsions will increase with increasing surface coverage Γ .

For sufficiently dense BNP layers, they can mimic a traditional, planar grafted brush of length L and coverage Γ , which must be greater than Γ considered above for mushrooms. Brush steric interactions are stronger than F_{steric} for mushrooms due to the stronger osmotic pressures produced upon confinement of a higher-density brush layers:

$$F_{brush} \approx k_B T L \Gamma^{\frac{3}{2}} \left[\left(\frac{2L}{D} \right)^{\frac{5}{4}} + \left(\frac{D}{2L} \right)^{\frac{7}{4}} \right] \quad (1.4)$$

This again highlights the strong role that coverage plays in determining the strength of repulsions. BNP layers are less likely to assume this form of a force law, but it is the idealize case for extremely dense particle packings with minimal roughness and curvature. We can also estimate the friction coefficient for overlapping brush layers¹⁰ assuming that shear forces are dominated by viscous drag of monomers in the weakly overlapping brush region and the force law of equation 1.4:

$$\mu_{eff} = \frac{\sigma_s}{F_{brush}} \approx \frac{6\pi\eta_{eff}v_s}{\Gamma k_B T} \left(\frac{D}{2L} \right)^{1/2} \quad (1.5)$$

This equation is the basis for most of the interpretation of polymer brush-mediated friction phenomena. Equation 1.5 predicts that the coefficient of friction will depend on the effective viscosity in the overlap region η_{eff} , sliding speed v_s , surface coverage, and separation distance. While adsorbed brush nanoparticles certainly do not follow this type of analytical expression in their friction behavior,

it still provides a physical picture for why high coverage brush layers with strong F_{brush} result in low friction coefficients.

Finally, patchy adsorbed BNP layers are capable of bridging across surfaces and forming particle-bridged adhesive contacts. Any BNP that is capable of adsorbing to a surface is capable of bridging across to an opposing surface of the same surface chemistry. Attractive bridging forces can be approximated by:

$$F_{bridge} \approx -4\pi R_p \gamma (L_c - D) \quad (1.6)$$

Which states that the bridging attraction increase linearly with distance starting at an onset distance associated with a characteristic size L_c of the bridging entity. In the case of BNP bridges, $L_p \sim R_p - R_c \sim L_{brush}$. The strength of the adhesive bridge γ depends on the nature of the particle-surface interaction (electrostatic, hydrogen bonding, etc). The net bridging force will result from the total number of bridging contacts within a contact radius A , or $\Gamma\gamma A$. Pure bridging assumes the particle layer is present on one surface and the opposing surface is bare. This condition of asymmetric surface coverage will be tested in the dissertation, but many of the conditions involve symmetric but less than saturation coverages and thus bridging adhesion is limited by some particle-particle repulsions.

1.4.3 Lubrication regimes and the Stribeck curve

Surfaces which are separated by an intervening viscous liquid film can be lubricated by three mechanisms, which are illustrated in **Figure 1.6** Error! Reference source not found. in the form of a Stribeck curve, a plot of friction coefficient vs. (viscosity) · (speed) / (pressure).

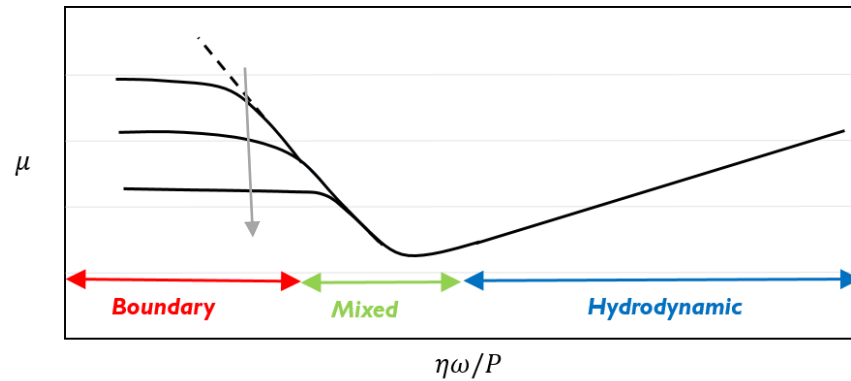


Figure 1.6. Stribeck curve for lubrication of a journal bearing shows the dependence of the friction coefficient μ on the non-dimensional quantity $\eta\omega/P$ with rotational speed ω , nominal bearing pressure P , and lubricant (Newtonian) viscosity η . Three identifiable lubrication regimes emerge: hydrodynamic, mixed, and boundary. The boundary lubrication regime is determined by the surface chemistry, where adsorbed layers control the limiting coefficient of friction.

At high $\eta\omega/P$ the sliding motion is completely supported by the viscous fluid, in what is called the hydrodynamic regime. As $\eta\omega/P$ decreases, the viscous fluid and the resulting lubrication forces are no longer able to support the applied load, and asperities on the surface begin to contact and the load is supported by both the surface and the fluid. This is called the mixed lubrication regime. Continuing to decrease $\eta\omega/P$ brings the surfaces into intimate contact and fluid properties no longer contribute to sliding motion, rather it becomes a function of the microscopic properties of the interfacial region formed between the surfaces. This is the boundary lubrication regime. In many cases, surface-adsorbed thin films dictate the efficacy of boundary lubrication and can either cause the surfaces to adhere (dashed line) or slide smoothly. The Stribeck curve, while developed for description of journal bearing performance, illustrates some of the major

mechanisms that govern frictional behavior in liquids, although this proposal will focus on the boundary lubrication regime.

1.4.4 *Friction from the macro- to the nano-scale*

Friction between contacting macroscopic surfaces generally obeys the empirical Amontons' Law, where the friction force between moving surfaces increases linearly with the applied load: $F_f = \mu F_n$, where μ is the friction coefficient, specific to the two opposing surfaces and the medium separating them. An important feature of Amontonian friction is the prediction that the friction force is independent of contact area. Real surfaces are not homogeneous, instead they are rough and contain asperities whose features can span length scales from the nano- to macro-scale. Yet, simulations⁵⁹ and experiments⁶⁰ have confirmed Amontons' Law to be independent of system size and applicable over a broad range of conditions. While the molecular picture of friction is still developing⁶¹, the coefficient of friction determined from Amontons' Law provides a useful metric for comparing frictional behavior between systems. For many systems there is a long-standing observation of positive-offset in F_f vs F_n , resulting in a modified^{58,62} Amontonian friction:

$$F_f = \mu F_n + F_{f,0} \quad (1.7)$$

where $F_{f,0}$ is the zero-load friction attributable to adhesive interactions. In its simplest form, $F_{f,0} = \sigma A$ with σ the interfacial shear stress and A the true contact area. At low applied loads ($F_n \rightarrow 0$), the adhesion force dominates friction, while at high loads the linear dependence with F_n is recovered. This friction behavior has been observed for bare surfaces of varying roughness separated by

hexadecane⁶³ and also for some polymer coated surfaces in water⁶⁴. The adhesion-controlled term could be further expanded in the context of Johnson-Kendall-Roberts (JKR)⁶⁵ or Derjaguin-Muller-Toporov (DMT)⁶⁶ theories of adhesive contact mechanics. Here, the non-linear friction behavior results from the non-linear area increase with applied load predicted in JKR theory. Thus, equation 1.7 could also take a form^{67,68}:

$$F_f = \mu(F_n + F_0) + \sigma\pi \left[\frac{R(F_n + F_0)}{K} \right]^{2/3} \quad (1.8)$$

Where F_0 is the pull-off force, R is the effective radius of curvature, and K is an effective elastic modulus in the contact area. K is not readily known for solvated polymer adlayers and introduces additional fitting parameters to any analysis performed via equation 1.8. In cases where strong hydration or electrostatic double layer repulsions are present, adhesion is greatly diminished and a linear-load dependence is recovered down to zero applied load. Most layers observed in this dissertation exhibit modified Amontonian friction of equation 1.7.

1.4.5 Polymeric boundary lubricants

Adsorbed and grafted polymer layers can be effective boundary lubrication agents, and good boundary lubricants will not only produce a low friction coefficient μ but also support sliding motion at high pressures. Friction between polymer layers is governed by a number of factors, such as the normal applied load, the sliding velocity, solution properties such as solvent quality and viscosity, and the chemical composition of a polymer, its mode of attachment to the surface, and the architecture of the surface-bound layer. The investigation of friction forces between polymer-bearing surfaces²⁰ has been a subject of many

experimental and theoretical/simulation^{69–71} investigations over the past 20 years. Generally, friction is reduced in systems where 1) the fluid medium is a good solvent for polymer, 2) a high density of chains on the surface reduce bridging interactions and 3) low mutual interpenetration between the layers reduces energy dissipation by chain rubbing⁷². Polyelectrolytes offer two major advantages over non-ionic polymers. First, mobile counterions contribute an additional repulsive osmotic pressure upon compression of polyelectrolytes, increasing repulsion between oppositely charged layers. Second, charged monomer units are surrounded by tenaciously bound hydration sheaths⁷³, and the improvement of chain sliding due to bound water, termed hydration lubrication⁷⁴ is believed to play an integral role in bio-lubrication processes.

Adsorbed polymers have had varying degrees of success as lubricants: chitosan⁷⁵ on a mica surface and silica probe ($\mu = 0.13$), mucin on a mica surface² and silica colloidal probe ($\mu = 0.03$), PEO⁷⁶ on silica surface and colloidal probe ($\mu = 0.03$ -0.3). However, friction coefficient almost always increases monotonically as the adsorbed homopolymer layers are further compressed due to chain interpenetration and rubbing between opposing loops and tails and also bridging interactions between the loose polymer ends and the opposing surface. This led to the development of bottle-brush polymers as lubricants, where cationic-*graft*-non-ionic bottle brushes electrostatically adsorbed to silica and mica have produced low friction coefficients and high load bearing capacity due to increased coverage and higher chain densities: poly-lysine backbone grafted with PEO chains⁷⁷, PLL-*g*-PEO adsorbed to silica surface and probe ($\mu = 0.035$ -

0.2 increasing with decreasing PEO length), charged methacryloxyethyl trimethylammonium chloride backbone grafted with 2000 molecular weight PEO side chains³⁵, PEO₄₅MEMA:METAC adsorbed to silica surface and probe ($\mu = 0.006$ -0.2, increasing with decreasing PEO fraction), and bottle-brush block copolymers consisting of cationic adsorbing blocks and bottle-brush lubricating buoys^{78,79}. Planar brushes have achieved some of the best lubricating properties, and of particular interest are: poly(acrylic acid) weak polyelectrolyte brushes¹⁸ on mica surface ($\mu = 0.1$ -0.3 at pH 5.5, increaseing with increasing salt concentration), PSGMA⁴² strong polyelectrolyte brushes ($\mu = 0.0005$), and zwitterionic⁴³ PMPC brushes on mica ($\mu = 0.0004$).

1.5 List of publications and manuscripts resulting from this dissertation

Saigal, T.; Riley, J.K.; Golas, P.L.; Bodvik, R.; Claesson, P.M.; Matyjaszewski, K.; Tilton, R.D. Poly(ethylene oxide) star polymer adsorption at the silica/aqueous interface and displacement by linear poly(ethylene oxide). *Langmuir* **2013**, 29, 3999-4007.

- The results are presented in Chapter 3. This work was begun by T Saigal, the majority of experiments and a portion of writing were performed by J.K. Riley.

Riley, J.K.; Matyjaszewski, K.; Tilton, R.D. Electrostatically controlled swelling and adsorption of polyelectrolyte brush-grafted nanoparticles to the solid/liquid interface. *Langmuir* **2014**, 30, 4056-4065.

- This work was completed during the second year prior to completion of the proposal exam. The results are presented in Chapter 4.

Riley, J.K.; An, J.; Tilton, R.D. Ionic surfactant binding to pH-responsive polyelectrolyte brush-grafted nanoparticles in suspension and on charged surfaces. *Langmuir* **2015**, *31*, 13680-13689.

- This work was completed during the third year in collaboration with Junxue An, a visiting student from KTH the Royal Institute of Technology in Stockholm Sweden. The results are presented in Chapter 6.

Riley, J.K.; Tilton, R.D. Surface forces between individual and mixed adsorbed layers of cationic polymer-brush nanoparticles and non-ionic star polymers. *Manuscript to be submitted*.

- This work was completed during the third and fourth year. The results are presented partially in Chapter 4 and partially in Chapter 7.

Lele, B.; Riley, J.K.; Tilton, R.D. Stability of colloidal suspensions using cationic polymer-brush grafted nanoparticles and cationic star polymers. *Manuscript to be submitted*.

- This work was completed by Bhagyashree Lele, a M.S. CPS student, under guidance and supervision of J.K. Riley during the fourth year. The results are not presented in this Dissertation, rather in the Masters' Thesis of B. Lele.

Riley, J.K.; Park, S.; Wang, Y.; Matyjaszewski, K.; Tilton, R.D. Aqueous lubrication using pH- and thermo-responsive block star polymers. *Manuscript in preparation*.

- This work was completed during the fifth year in collaboration with Sangwoo Park and Yi Wang in the Matyjaszewski group, Department of Chemistry, CMU. The results are presented entirely in Chapter 8.

Riley, J.K.; Tilton, R.D. Controlling surface forces through temperature and pH-induced hysteretic adsorption of polyelectrolyte brush-grafted nanoparticles. *Manuscript in preparation*.

- This work was completed during the fourth and fifth year. The results are presented in Chapter 4, Chapter 5, and Chapter 9.

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2. Materials, methods, and experimental techniques

2.1 Polymer brush nanoparticles

All polymer brush nanoparticles are synthesized by Atom Transfer Radical Polymerization (ATRP) in collaboration with the research group of Professor Krzysztof Matyjaszewski in the Department of Chemistry, Carnegie Mellon University. Brief summaries of material syntheses and characterization are provided in this chapter, with references to include previously published synthetic procedures from our group where appropriate. For materials created specifically as a result of this thesis, the detailed synthesis procedure will be included in the associated major content chapter later on.

2.1.1 *Core-crosslinked PEO star polymers*

Non-ionic star polymers based on poly(ethylene oxide) are synthesized by the core-crosslinking of macromonomers method. The detailed synthesis and characterization are published in previous work from our group^{1,2}. Briefly, poly(ethylene oxide) methyl ether methacrylate macromonomer (PEO₄₅MA) with $M_n = 2080$ (degree of polymerization, $DP = 45$) and $M_w/M_n = 1.05$ is reacted in the presence of a di-functional divinyl benzene (DVB) crosslinker under ATRP conditions. The resulting material has a densely cross-linked core surrounded by a hydrophilic corona of PEO₄₅MA arms.

Table 2.1. Macromolecular characterization of core-crosslinked PEO star polymers.

Star polymer type	M_w, MALLS	f	σ_{app} (nm^{-2})
PEO ₄₅ MA- <i>co</i> -DVB (aggregates in water)	1.12×10^6	450	0.44
PEO ₄₅ MA- <i>co</i> -DVB (dispersed in DMF)	1.76×10^5	64	0.50

2.1.2 PDMAEMA grafted silica nanoparticles

Polyelectrolyte-grafted nanoparticles are synthesized by the “grafting from” method using surface-initiated ATRP (SI-ATRP). Detailed synthesis, purification, and particle characterization has been published previously in our group. Silica nanoparticles are first coated with a mixed silane layer consisting of dummy initiator and active ATRP initiator, resulting in a controlled grafting density on the particle surface. 2-(dimethylamino)ethyl methacrylate (DMAEMA) is polymerized in the presence of the initiator-functionalized silica nanoparticles using traditional ATRP to form SiO₂-*g*-PDMAEMA brush-grafted nanoparticles. PDMAEMA is a weakly cationic polyelectrolyte whose degree of protonation depends on the pH and ionic strength of the surrounding aqueous solution. Additionally, PDMAEMA exhibits a lower critical solution temperature (LCST) in aqueous solution. The LCST is tied to the charge density of PDMAEMA, and accordingly the LCST also depends on pH. The dual-responsive nature of PDMAEMA imparts both pH and thermal responsiveness to SiO₂-*g*-PDMAEMA nanoparticles. The particle characteristics are tabulated below, and examples of particle pH and thermal response are shown below:

Table 2.2. PDMAEMA brush grafted nanoparticle properties.

D_{core} (nm)	σ (nm ⁻²)	$M_{w, arm}$	M_w/M_n
20.0	0.46	2.3×10^4	1.25
15.4	0.22	2.5×10^4	1.31

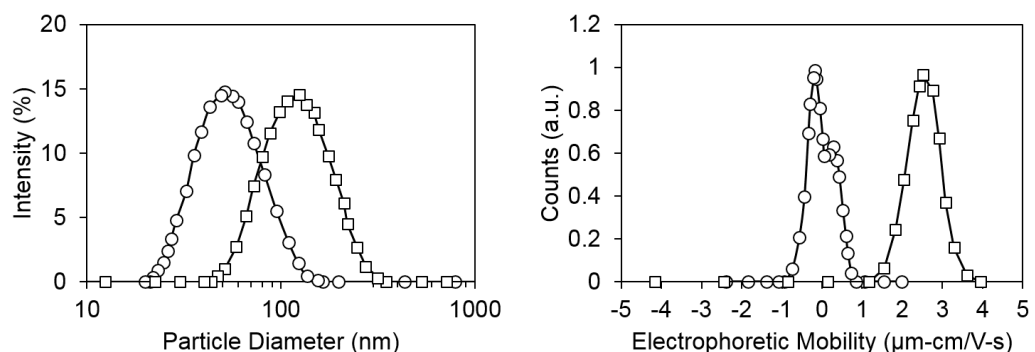


Figure 2.1. Particle size and electrophoretic mobility distributions for 1.0 mg/mL SiO₂-*g*-PDMAEMA suspensions in 10 mM NaCl. (□) pH 5.2 and (○) pH 9.1. SiO₂-*g*-PDMAEMA have a grafting density of 0.22 chains/nm² and arm molecular weight of 25,000.

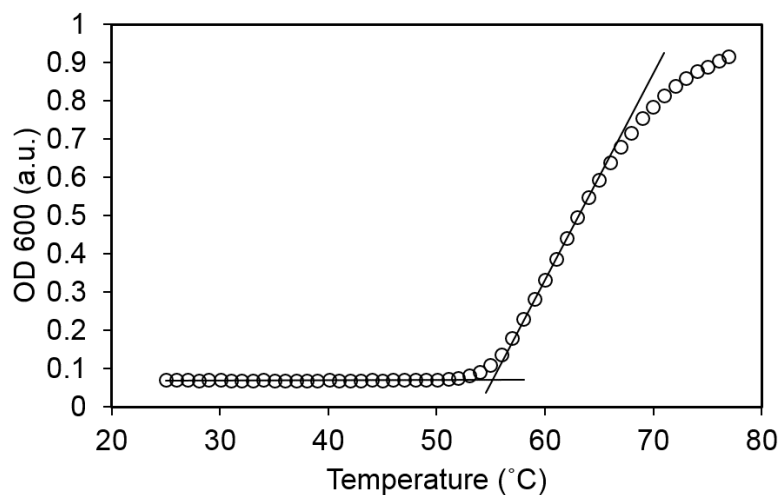


Figure 2.2. Turbidity measurement to determine the critical flocculation temperature of a 1.0 mg/mL SiO₂-*g*-PDMAEMA suspension in 1 mM NaCl, pH 8.5 at a heating rate of 1 °C/min. The CFT is measured to be 55 °C

2.1.3 *β -cyclodextrin-core star polymers*

β -cyclodextrin (β -CD) – a cyclic carbohydrate consisting of 7 linked sugar groups – was used as a precursor for synthesizing a series of novel block-arm star polymers by the “grafting from” ATRP method. The full synthesis procedure and characterization of the new polymers is detailed in full in Chapter 9. Briefly, β -CD is functionalized with 14 ATRP initiator moieties by a selective transesterification reaction. Star polymers are then synthesized under conventional ATRP reaction conditions to generate 14-arm star polymers with well-defined structure. Homopolymer stars are synthesized from the first ATRP reaction off the initiator-functionalized β -CD core. The homopolymer stars retain a reactive halide end group that can be re-initiated in a chain extension reaction to generate block copolymer stars. Star polymers are synthesized from the following set of monomers: di(ethylene glycol) methyl ether methacrylate (MEO₂MA), 2-(dimethylamino)ethyl methacrylate (DMAEMA), and 2-methacryloyloxyethyl phosphorylcholine (MPC). MEO₂MA is polymerized to PMEO₂MA, a non-ionic polymer which exhibits a lower critical solution temperature (LCST) of 29 °C in water. DMAEMA is polymerized to PDMAEMA, a weakly cationic polyelectrolyte whose degree of protonation depends on the local pH and salt concentration of the aqueous solvent. PDMAEMA also exhibits an LCST in water, however its LCST depends on the charge density of the polymer and thus depends strongly on pH. MPC is polymerized to PMPC, a zwitterionic polymer containing both positively and negatively charged groups on each monomer but remaining net electrostatically neutral. Thus, block copolymer stars can be

synthesized using these monomers to generate novel multi-responsive, water soluble polymeric materials. We have synthesized homo-, diblock-, and triblock-star polymers from this monomer set. The following nomenclature is used to identify the materials: β -CD-(A-*b*-B-*b*-C)₁₄, where A, B, and C represent the discrete polymer blocks.

Table 2.3. Synthesized 14-arm star polymers with degree of polymerization.

Star polymer type	<i>DP A</i>	<i>DP B</i>	<i>DP C</i>
β -CD-(PDMAEMA) ₁₄	45	X	X
β -CD-(PMEO ₂ MA) ₁₄	62	X	X
β -CD-(PMPC) ₁₄	54	X	X
β -CD-(PMEO ₂ MA- <i>b</i> -PDMAEMA) ₁₄	50	34	X
β -CD-(PMEO ₂ MA- <i>b</i> -PDMAEMA- <i>b</i> -PMPC) ₁₄	50	34	17

2.2 Experimental methods and technique

This section details the primary experimental methods used to study the properties of polymer brush nanoparticles used in this dissertation. The experimental techniques can be classified as either bulk or interfacial characterization methods. Bulk suspension properties are primarily evaluated using a variety of light scattering techniques. The variant light scattering methods are used to probe particle size, charge, aggregation, and molecular weight characteristics of the polymer brush nanoparticles and associated polymeric or nanoparticulate materials. Almost all polymer brush nanoparticles are characterized under dilute or, rarely, semi-dilute suspension conditions. The interfacial properties of polymer brush nanoparticles are evaluated using a number of surface sensitive measurement techniques. Ellipsometry and quartz crystal

microbalance with dissipation are used to evaluate the *in-situ* adsorption kinetics and extent of adsorption of polymer brush nanoparticles on solid substrates. Atomic force microscopy is used to probe the surface topography of adsorbed layers in imaging mode and also to evaluate colloidal and polymeric surface forces using the colloidal probe method. Streaming potential measurements are used as a complimentary method to characterize nanoparticle adsorption and interfacial electrokinetic behavior.

2.2.1 *Light Scattering*

2.2.1.1 Dynamic light scattering

Dynamic light scattering (DLS) measurements are performed on a ZetaSizer ZSP (Malvern Instruments) instrument. DLS is used to determine the hydrodynamic size of polymer brush nanoparticles by measuring their Brownian diffusion in suspension. DLS is appropriate for measuring particle sizes in the range $\sim 1 \text{ nm} - 1 \text{ }\mu\text{m}$, and all polymer brush nanoparticles studied here fall in this size range. DLS involves measuring the intensity of light scattered from a particle or macromolecule suspension as a function of time at a fixed angle of detection. Brownian motion of the suspended particles will cause fluctuations in the scattered light intensity, and the frequency, amplitude, and dynamic evolution of these fluctuations can ultimately be related to the diffusion coefficient of an ensemble of scattering entities. The dynamic information is derived from the autocorrelation function for the intensity of scattered light. The simplest analysis assumes an exponential decay in the autocorrelation function $g^1(q; \tau)$, where the

decay rate Γ_1 can be related to the wave vector q and translational diffusion coefficient D_z :

$$\begin{aligned} g^1(q; \tau) &= \exp(-\Gamma_1 \tau) \\ \Gamma_1 &= q^2 D_z \end{aligned} \tag{2.1}$$

The hydrodynamic radius R_h of the particles is calculated from the measured z-average diffusion coefficient by the Stokes-Einstein relation:

$$R_h = \frac{k_B T}{6\pi\eta D_z} \tag{2.2}$$

In practice, most samples exhibit polydispersity and the autocorrelation function is a sum of exponential contributions from scatterers of different size. Thus, fitting autocorrelation function data requires more complicated numerical algorithms, such as the CONTIN or cumulants method.

DLS is particularly sensitive to size polydispersity of the suspended particles, so care is taken to prevent dust accumulation in the measurement system. Most solutions are filtered through 0.2 μm diameter filters prior to measurement and handled carefully to minimize ambient lab air exposure. It should be noted that the hydrodynamic size of polymer brush nanoparticles is not the exact physical size of the particle. Brush nanoparticles bear a polymeric layer that is permeable to solvent flow, and thus the plane of shear is not well defined. The measured hydrodynamic radius is particularly sensitive to the distribution of polymer chains, adding uncertainty for non-uniform or polydisperse polymeric coatings. However, the hydrodynamic radius is a suitable descriptor for relative changes in particle size.

2.2.1.2 Electrophoretic light scattering

Electrophoretic mobility measurements are performed on a ZetaSizer ZSP (Malvern Instruments) dynamic light scattering instrument. Mobility measurements are performed in disposable folded capillary cells (Malvern, model DTS 1070). The cell bears two gold electrodes that enable a voltage drop to be applied across the capillary cell while scattering data is obtained. The electrophoretic mobility is measured by a combination of laser-doppler microelectrophoresis and phase-angle light scattering. The basis of this technique involves comparing the frequency of incident light to the frequency of scattered light in the presence of an oscillating applied electric field. A phase shift will occur if the particles travel with a velocity relative to the direction of the biased electric field. The electrophoretic mobility of the scattering entities is extracted from the measured phase shift. The measured electrophoretic mobility, defined as the particle velocity v divided by the strength of the applied electric field E , is related to the particle zeta potential for spheres by the generalized von Smoluchowski equation:

$$\mu_E = \frac{v}{E} = \frac{\epsilon\epsilon_0\zeta}{\eta} f(\kappa a) \quad (2.3)$$

where ϵ is the fluid dielectric constant, ϵ_0 is the permittivity of free space, ζ is the zeta potential, η is the fluid viscosity, and $f(\kappa a)$ is the Henry function, which can be approximated well for a given particle radius a by the analytical expression derived by Ohshima³:

$$f(\kappa a) = \frac{2}{3} \left[1 + \frac{1}{2 \left(1 + \frac{2.5}{\kappa a (1 + 2e^{-\kappa a})} \right)^3} \right] \quad (2.4)$$

In the limit of small κa , $f(\kappa a) \rightarrow 1.5$ and the mobility expression reduces to the Smoluchowski equation. In the limit of large κa , $f(\kappa a) \rightarrow 1.0$ and the mobility relation reduces to the Hückel equation. Most of the polymer brush nanoparticles studied in this dissertation have intermediate κa and require the use of the Henry function to approximate the zeta potential from the measured electrophoretic mobility.

2.2.1.3 Turbidity

Turbidity measurements to determine the critical flocculation temperature (CFT) or cloud point temperature (CPT) of polymer and brush nanoparticle solutions are performed on a Cary Bio 300 UV-Vis spectrophotometer (Agilent) equipped with a temperature controller. Almost all materials studied in this dissertation do not absorb light in the visible spectrum, so a wavelength of 500 – 600 nm is selected to track relative changes in turbidity, or optical density.

Polymer solutions or colloidal suspensions are placed in a capped quartz spectrophotometry cell and subjected to a temperature program that includes heating and cooling cycles while measuring the transmittance of light through the cell. Typical heating occurs from 22 °C to 95 °C at a heating rate of 1 °C/min. Cooling occurs back to room temperature typically at a rate of 2 - 3 °C/min. The

LCST/CFT/CPT is calculated as the inflection point in a plot of optical density versus temperature.

2.2.2 Phase-modulated ellipsometry

Optical thickness and surface excess concentrations were measured *in situ* using phase modulation ellipsometry on a Picometer Ellipsometer (Beaglehole Instruments, New Zealand). This method detects adsorption by the change in ellipticity ρ of a polarized laser beam upon reflection from a surface, when incident at angle ϕ . The ellipticity ρ is defined as the ratio of the complex reflection coefficients of the parallel polarized r_p , and perpendicular polarized r_s , components of the beam:

$$\rho = \frac{r_p}{r_s} = \tan \Psi e^{i\Delta} = \text{Re}(\rho) + i\text{Im}(\rho) \quad (2.5 - 6)$$

$$\text{Re}(\rho) = \tan \Psi \cos \Delta \quad ; \quad \text{Im}(\rho) = \tan \Psi \sin \Delta$$

Ellipsometry data is often interpreted in terms of the ellipsometric angles Ψ and Δ . The imaginary part of ρ is directly proportional to the surface excess polarizability, deriving from finite adlayer thicknesses or surface heterogeneity. Following the Beaglehole convention used in our instrumentation, the signal of the phase modulated ellipsometer is represented by x and y parameters, defined as:

$$x = \text{Re}(\rho) \frac{2}{1 + \text{Re}(\rho)^2 + \text{Im}(\rho)^2} \quad (2.7 - 8)$$

$$y = \text{Im}(\rho) \frac{2}{1 + \text{Re}(\rho)^2 + \text{Im}(\rho)^2}$$

The y parameter is particularly sensitive to changes in optical properties of interfacial films. This data treatment is less susceptible than traditional null

ellipsometry to small errors in incident angle close to the Brewster angle, where thin film sensitivity is greatest. The incident angle was usually set to 70-72°, near the Brewster angle for water/silicon, for all measurements. Single side polished silicon wafers with a 2-3 nm native oxide layer (International Wafer Services, Inc.) were oxidized in an air-fed furnace at 1000°C for 20 minutes to produce a 40 - 45 nm SiO₂ layer, verified by ellipsometry for each wafer. Prior to all experiments, the surface oxidized wafers were cleaned as described previously⁴, rendering them hydrophilic. All wafers were stored in de-ionized water and used within 2 h.

Analyzing ellipticity changes according to a homogeneous four-layer surface model (bulk silicon + oxide layer + adsorbed layer + bulk solution) yields the optical average thickness d_l and refractive index n_l of the adsorbed layer, from which the surface excess concentration Γ is calculated from the DeFeijter relation⁴¹

$$\Gamma = d_l \frac{n_l - n_0}{dn/dc} \quad (2.9)$$

with n_0 the bulk refractive index. The refractive index increment of the polymer solution dn/dc was determined by differential refractometry for all materials. An accurate measurement of dn/dc is necessary for quantitative surface excess concentration calculations. Typically, $dn/dc \approx 0.11 - 0.15$ mL/g for polymers in aqueous solution. TF Companion software (Version 3.0, Semicon Software Inc.) was used for ellipsometry analysis. The optical average thickness of the adsorbed layer was determined from the value of y obtained after it had reached a steady value. The adsorbed layer is the only one with an unknown refractive index. Thickness values were determined assuming one of three possible adsorbed layer refractive indices, either $n_l = 1.37$, 1.40 or 1.5, spanning a reasonable range of

values between pure water (1.333) and pure polymers (1.5). The optical thickness and refractive index of the adsorbed layer are highly coupled so that their individual values are highly model-dependent for very thin films, but their errors are mutually compensating and the quantity $d_I(n_I - n_o)$ is nearly invariant, with the result that the surface excess concentration is nearly independent of the optical assumptions. The assumed value of n_I had only a minor effect on Γ , usually within 5%.

2.2.3 Quartz crystal microbalance with dissipation

Quartz crystal microbalance with dissipation (QCM-D) adsorption measurements are performed on a Q-Sense E4 instrument (Biolin Scientific). Quartz resonators with sputtered silica surfaces (QSX 303, 50 nm SiO₂) and fundamental resonance frequency of 4.95 MHz are utilized as adsorption substrates. QCM-D sensors are cleaned by sonication in RBS detergent, rinsing with de-ionized water, sonicating in 2 wt% sodium dodecyl sulfate, SDS, solutions, rinsing with water, drying in nitrogen gas, and UV-ozone treatment for 30 minutes. This leaves the surface of the substrates uniformly hydrophilic. A peristaltic pump (Ismatec Inc.) is used to flow liquids through Teflon tubing to the QCM-D flow cell and sensor, and typical flowrates are 0.1 – 0.5 mL/min.

QCM-D is a surface sensitive technique that is widely used to sense changes in mass that are coupled to an oscillating quartz crystal. For this dissertation, QCM-D is used to measure the adsorbed mass and viscoelastic properties of adsorbed polymer brush nanoparticle layers. QCM-D continuously measures the resonance frequency f and dissipation factor D during pulsed-oscillation of a piezoelectric sensor. The dissipation factor is measured by

switching off the applied voltage that drives the oscillations, and monitoring the decay of the oscillation amplitude. Damped oscillations are attributed to energy loss, and the dissipation factor is defined as:

$$D = \frac{2}{f\tau} = \frac{E_D}{2\pi E_s} \quad (2.10)$$

Where τ is the decay time of the oscillations, E_D is the dissipated energy, and E_s is the stored energy over one oscillation period.

QCM-D data can be modeled to a first approximation by the Sauerbrey equation, which states that the the adsorbed mass coupled to the sensor Γ_{SB} is proportional to the frequency shift Δf_n

$$\Gamma_{SB} = -\frac{C \Delta f_n}{n} \quad (2.11)$$

Where n is the overtone number and C is quartz material property, or the sensitivity. For the quartz crystals used in this work (fundamental resonance frequency $f_F = 5$ MHz), $C = 0.18 \text{ mg m}^{-2} \text{ Hz}^{-1}$. Thus, for a typical frequency shift of 40 Hz, the adsorbed mass is 7.2 mg/m^2 . The Sauerbrey analysis is only valid for rigid, homogeneous adsorbed layers. A more stringent criterion states that the Sauerbrey model is valid when the dissipation shift is less than 10% of the measured frequency shift (in units of Hz). Additionally, any spreading or dispersion in data for different overtones suggests that the Sauerbrey model is not valid.

The majority of materials investigated in this dissertation are polymeric and produce layers that are viscoelastic in nature. Adsorbed viscoelastic layers

dissipate energy, and thus produce measurable frequency and dissipation shifts upon adsorption to the sensor. The frequency and dissipation shifts are a complex function of the fluid properties, adsorbed mass, and layer viscoelastic properties. Conventional viscoelastic modeling in QCM-D utilized the Voigt-Kelvin model to represent the properties of the adsorbed layer by independent elastic and viscous contributions. In the Voigt model, the layer is characterized by its thickness d_f and density ρ_f , and has a complex shear modulus μ^* of the form:

$$\mu^* = \mu' + i\mu'' = \mu_f + i2\pi F\eta_f \quad (2.12)$$

The frequency and dissipation shifts Δf_n and ΔD_n for this type of film are then dependent on the quartz resonator thickness and density, t_q and ρ_q ; film thickness, viscosity and shear modulus, d_f , η_f and μ_f ; and bulk solution density and viscosity, ρ_B and η_B . The extension of Voigt model to QCM-D analysis was derived by Voinova⁵, and the expressions for the frequency and dissipation shifts are shown below:

$$\begin{aligned} \Delta F &= -\frac{1}{2\pi t_q \rho_q} \left\{ d_f \rho_f \omega - 2d_f \frac{\eta_f \omega^2}{\mu_f + \omega^2 \eta_f^2} \left(\frac{\eta_B}{\delta} \right)^2 \right\} \\ \Delta D &= -\frac{1}{2\pi F t_q \rho_q} \left\{ 2d_f \frac{\eta_f \omega}{\mu_f^2 + \omega^2 \eta_f^2} \left(\frac{\eta_B}{\delta} \right)^2 \right\} \end{aligned} \quad (2.13 - 14)$$

The parameter δ is the viscous penetration depth of the acoustic wave. The QCM-D data is fit numerically to the Voigt model above to provide the adsorbed mass $\Gamma_{voigt} = d_f \rho_f$, shear modulus μ_f , and layer viscosity η_f . It is important to note that adsorbed mass determined from QCM-D is the sensed mass consisting of contributions from the polymer and any hydrodynamically coupled solvent.

2.2.4 *Simultaneous QCM-D/Ellipsometry*

Ellipsometry and QCM-D measurements performed in tandem are a powerful method for characterizing the properties of adsorbed, viscoelastic layers. An important difference between ellipsometry and QCM-D for studying adsorbed layers is that ellipsometry detects changes in total adsorbate mass on the substrate while QCM-D measures the viscoelastic properties of the adsorbate mass and the solvent that is hydrodynamically trapped in the adsorbed layer and coupled with the sensor motion during shear oscillation. Combining ellipsometry and QCM-D can then estimate the relative amounts of adsorbate and solvent that is coupled to an adsorbed layer, which can be a valuable piece of information in lubrication of adsorbed layers. It is also a more accurate method of characterizing heterogeneous adsorbed layers, such as low-coverage brush nanoparticles, compared to QCM-D used by itself.

The general procedure for analysis of ellipsometry data follows from the section above, and slight alterations made for simultaneous QCM-D/ELL measurements have been adopted from Bodvik and co-workers⁶. First, a variable-angle ellipsometry scan of the QSX 335 sensor is done in air to determine the baseline optical properties of the sensor. Here, the 100 nm titanium layer is treated as a semi-infinite medium characterized by its complex refractive index at 632.8 nm and the TiO₂ and SiO₂ layers are combined into a single effective oxide layer whose refractive index is dominated by SiO₂. We fit the variable angle measurement to determine the effective oxide layer thickness. Once the underlying substrate is characterized, adsorption is modeled using a four-layer

optical model comprised of 1) bulk titanium, 2) effective TiO₂/SiO₂ layer, 3) adsorbed layer, and 4) bulk solution. The fit for the equivalent thickness of the adsorbed layer assuming a refractive index of $n_{ads}=1.44$ and bulk solution refractive index $n_{liq}=1.333$. The ellipsometry surface excess concentration is calculated from the equivalent thickness and assumed refractive index via the De Feijter relation.

2.2.5 Atomic Force Microscopy

Atomic force microscopy (AFM) is a scanning probe technique developed in the 1980's by Binnig to map micro-, nano-, and molecular scale topography on solid surfaces. In the decades since, AFM has evolved into a versatile and extremely powerful instrument with standard applications in physics, chemistry, materials, and biology. Conventional AFM employs a microcantilever with a sharp ($\sim 1\text{-}10$ nm radius of curvature) tip as a force transducer and detects tip-surface interaction forces by monitoring the cantilever deflection via an optical lever and photodiode. In traditional operating modes, such as contact mode and tapping mode), a set-point force (or amplitude) is specified by the user and a feedback controller maintains the set point force by moving the sample up and down relative to the tip via a piezoelectric scanner. The major components of an AFM instrument are depicted in **Figure 2.3**. The force resolution of AFM is typically ~ 5 pN and vertical displacements < 1 nm can be achieved by the piezoelectric scanner.

In this dissertation, AFM was used for both topographical imaging and surface force evaluation. Measurements were performed on a Bruker Multimode

VIII AFM equipped with a Nanoscope V controller. Image processing and force curve analysis are performed using the Nanoscope Analysis 1.5 software program.

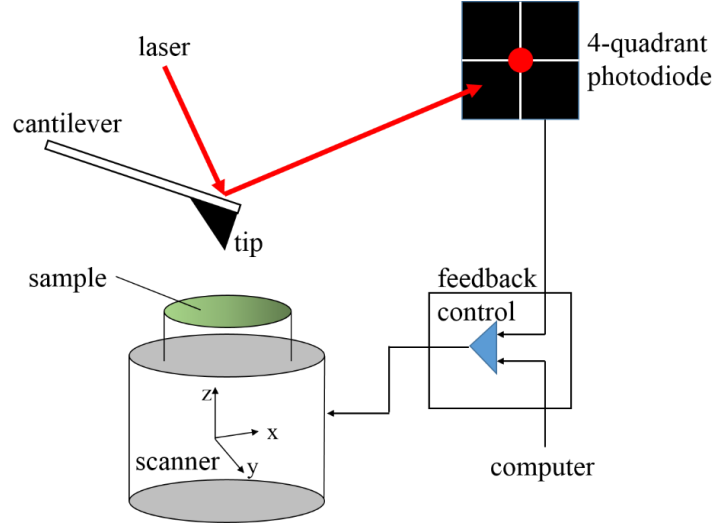


Figure 2.3. Schematic of an atomic force microscope and major components.

2.2.5.1 Colloidal probe force measurements

Normal and lateral forces are measured between a flat substrate and a micron-sized sphere using the colloidal probe technique. This method was introduced by Ducker and coworkers⁷ as a means to evaluate colloidal surface forces using AFM. The colloidal probe technique differs from traditional AFM only in the type of cantilever and tip employed. Traditional AFM cantilevers have very sharp tips in order to enhance imaging resolution. Alternatively, colloidal probe cantilevers typically consist of a tipless cantilever that has a sphere with a radius R_{CP} of 1 – 20 μm secured to its end. In most applications the separation D between the colloidal sphere and the surface is $D \sim 1\text{-}100\text{ nm}$, resulting in the condition $D/R_{CP} \ll 1$. This condition allows colloidal probe force-distance

profiles $F_n(D)$ to be converted to interaction energy per unit area via the Derjaguin approximation:

$$F_n(D) \approx 2\pi R_{CP} E(D) \quad 2.15$$

Thus allowing AFM to measure not only interaction forces⁸, but also to evaluate total interaction energy profiles between surfaces and adsorbed polymer layers.

Colloidal probes are assembled manually by gluing a micron-sized sphere to the end of a tipless AFM cantilever using a micromanipulator and inverted microscope. The procedure for fabricating a colloidal probe cantilever is as follows:

1. Power on inverted microscope.
2. Deposit the desired microspheres onto a clean glass microscope slide. If microspheres are in the form of a liquid suspension, then spread a droplet onto the slide and gently blow air until the liquid is evaporated.
3. Place a small drop of UV-curable epoxy (NA-63, Norland Adhesives) on a separate clean glass microscope slide. Smear the epoxy from the drop into thin fingers or spots using a small-diameter wire or syringe needle. Thin spots or streaks of epoxy are more easily accessible for the cantilever than a large pool.
4. Cut a thin PDMS gel pad strip from an AFM cantilever box, and glue the strip to the micromanipulator arm. The PDMS pad should be kept clean or replaced frequently, since dust accumulation will weaken the adhesion of the cantilever to the pad.

5. Place the tipless cantilever on the PDMS padded micromanipulator arm.
Position the cantilever such that it overhangs the edge of the micromanipulator arm, but is sufficiently in contact with the pad to ensure strong adhesion. Install the arm with cantilever onto the micromanipulator and align into view of the microscope under low magnification.
6. Place the microscope slide with epoxy onto the microscope stage. Locate a thin streak or spot of epoxy under high magnification, then switch to a low-magnification objective and manually position close to the slide but above the glue spot.
7. Bring the cantilever close to the epoxy. Once the tipless cantilever of interest is positioned directly over the epoxy, quickly dip and withdraw the cantilever from the epoxy.
8. Move to a clean spot on the microscope slide and press the cantilever against the surface repeatedly to remove excess epoxy. Only a small amount of epoxy is required to pick up a microsphere, and too much epoxy on the cantilever will creep around the colloidal sphere and contaminate the underside of the particle.
9. Raise the micromanipulator arm and replace the epoxy microscope slide with the slide coated with dry microspheres.
10. Locate an isolated microsphere and position the cantilever with glue directly above the microsphere. Lower the cantilever until it is in close vicinity of the microsphere. Ensure the cantilever is centered above the

particle, then lower the arm and pick up the particle. The particle should readily attach the cantilever with sufficient, but not excessive, glue.

11. Remove the cantilever from the micromanipulator arm. Cure the epoxy by treating it with UV-Ozone for 30 minutes. This will also cleanse the cantilever surface of organic contaminants.

12. The cantilever is ready to mount and use. See Figure 2.4 for an image of a prepared cantilever.

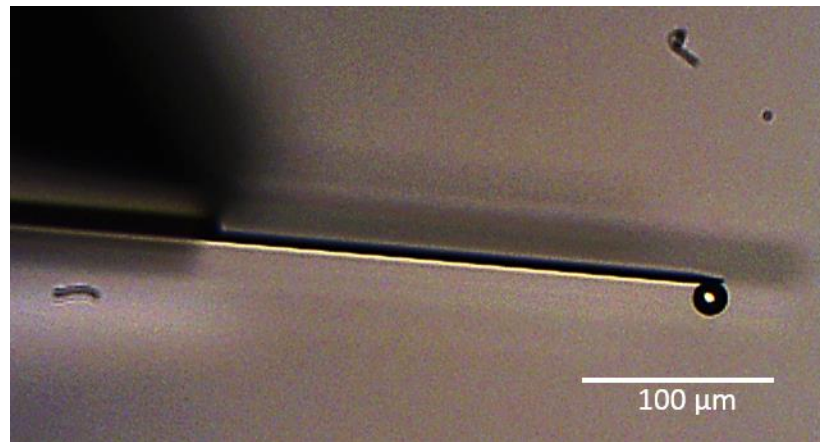


Figure 2.4. Microscope image of a colloidal probe cantilever. Cantilever: HQ:CSC38/tipless/Cr-Au (C-lever, Mikromasch), with nominal length of 250 μm . Sphere: 19.8 μm diameter silica (Corpuscular Inc.) attached via UV-curable adhesive (NA-63, Norland Adhesives).

Colloidal probe measurements are conducted with a PF-type closed loop z scanner and additional PicoForce controller. This enables precise and accurate control over the approach and retract of the surfaces and is essential for quality force curve measurement and evaluation. Normal forces are measured from the displacement of the cantilever as:

$$F_n = k_z \delta_z (V_z - V_0) = \alpha \Delta V_z \quad 2.16$$

Here, k_z is the normal spring constant in units of [N/m], δ_z is the normal photodiode sensitivity in units of [m/V], and $\Delta V = V_z - V_0$ is the photodiode detected cantilever deflection relative to the zero-force voltage in units of [V]. The normal photodiode sensitivity is determined from the constant compliance force region upon pressing a bare probe against a bare surface. Typically, $\delta_z \sim 50 - 70 \text{ nm/V}$. α is the overall conversion factor from raw voltage to normal force.

Friction forces measured by AFM take a similar form:

$$F_f = \frac{k_t}{2H_{eff}\delta_{lat}} (V_{lat}^+ - V_{lat}^-) = \beta \frac{\Delta V_{lat}}{2} \quad 2.17$$

Here, k_t is the torsional spring constant in units of [N m], H_{eff} is the lever-arm height or the diameter of the colloidal probe plus the thickness of the cantilever in units of [m], δ_{lat} is the lateral photodiode sensitivity, and $\Delta V_{lat} = V_{lat}^+ - V_{lat}^-$ is difference between the average friction force on trace and retrace of the raster scanned probe in units of [V]. The lateral photodiode sensitivity was determined by the test-probe method⁹ to be 3650 V/rad, in good agreement with the sensitivity measured by the AFM head tilting method¹⁰ reported in the literature. The normal and torsional spring constants are measured by fitting the thermal noise power spectrum for normal or torsional bending to a damped harmonic oscillator model. The spring constants are calculated from the quality factor, resonance frequency, and plane-view dimensions of the cantilever via the Sader method¹¹. The torsional spring constant k_t also be calculated from the measured normal spring constant by the hybrid method of Alvarez-Asencio and coworkers¹²

for rectangular cantilevers. Here, k_t is calculated from the experimentally determined k_z through classic beam and plate theory. A summary of colloidal probe cantilevers and their properties is given:

Table 2.4. Summary of colloidal probe cantilever properties

Cantilever type	L (μm)	w (μm)	t (μm)	k_z (N/m)	k_t (N m)	Probe type	β (nN/mV)
Mikromasch, CSC-tipless <i>c</i> -lever	300	32.5	1.0	0.08 - 0.10	3.5E-9	10 μm glass	0.0769
						20 μm silica	0.0435
Bruker MLCT-tipless <i>b</i> -lever	200	15	0.5	0.02 – 0.04	7.0 E-10	10 μm glass	0.0091
						20 μm silica	0.0048

2.2.5.2 Imaging

AFM images are obtained in either tapping mode or ScanAsyst mode using a vertical-engage J scanner and Bruker Multimode VIII AFM. AFM images are obtained based on the corrective movement of the piezoelectric scanner as it attempts to maintain a user-defined force threshold. Imaging in air is performed using sharp-tip, ScanAsyst-Air cantilevers with nominal radius of curvature of 10 nm. Imaging in liquid is performed using ScanAsyst-Fluid+ cantilevers with a nominal tip radius of curvature of 2 nm. PeakForce Quantitative Nanomechanical Mapping ® (PF-QNM) experiments are performed using the automated Bruker software to analyze force curves and extract spatial maps of adhesion, deformation, modulus, and dissipation. Refer to previous work in our group for a full description of this technique as applied to mechanical mapping of individual brush particles¹³.

2.2.6 Streaming potential

Streaming potential measurements were conducted using the ZetaSpin (Zetamatrix Inc.) rotating disk method. An oxidized and cleaned 2.5 cm diameter silicon wafer was rotated at 4000 rpm in the electrolyte solution, generating a streaming potential along its surface. The measured streaming potential was measured using a silver electrode near the center of the surface relative to a silver/silver chloride reference electrode far away from the surface in the electrolyte reservoir. The measured streaming potential can be converted to the surface zeta potential via the analysis of Sides and co-workers.^{14,15}

$$\zeta_s = \frac{1.96\kappa_i\nu^{1/2}}{\varepsilon a_{disk}\Omega^{3/2}} \frac{1}{2 \left(1 - z/a_{disk} - \frac{1}{2(z^2/a_{disk}^2 + 1)^{1/2}} \right)} \phi_s \quad 2.18$$

with bulk solution ionic conductivity κ_i , kinematic viscosity ν , and dielectric constant ε , surface-electrode separation distance z , disk radius a , and rotational speed Ω . The zeta potential measured here is valid for a sharp interface, and thus errors are introduced when analyzing polymer brush nanoparticle-coated surfaces. However, the measured streaming potential is almost always indicative of the sign of the surface charge of the layer.

2.3 References

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3. Adsorption of polyethylene oxide star polymers to the silica/water interface

Multi-arm star copolymers with 2000 molecular weight poly(ethylene oxide) arms, synthesized via atom transfer radical polymerization (ATRP) of PEO-methacrylate (PEOMA) macromonomers in the presence of divinyl benzene (DVB) crosslinkers, are an example of molecular or nanoparticulate brushes that are of interest as steric stabilizers or boundary lubrication agents when adsorbed from solution to a solid/aqueous interface. In this study, ellipsometry and quartz crystal microbalance with dissipation were used to measure adsorption at the silica/aqueous interface for linear and star PEO polymers.

First, adsorption isotherms are measured for both linear PEO and star PEO of comparable molecular weights. The compactness of the PEO star polymers (molecular weight 1.2×10^6) yields a saturation surface excess concentration that is approximately 3.5 times greater than that of the high molecular weight (1×10^6) linear PEO. Competitive adsorption measurements are performed to evaluate the preferential adsorption of star and linear PEO polymers based on their relative entropic adsorption penalties.

Star and linear PEO adsorption is also measured as a function of solution pH to investigate the role of hydrogen bonding on the extent of adsorption of the PEO based materials on silica surfaces. A sharp pH-induced adsorption cutoff is discovered near pH 9.2 – 9.5 for both linear and star PEO, corresponding to a decreased population of hydrogen bonding silanol groups on the surface. The role of surface charge and ion composition is further probed by studying the adsorption of star PEO in the presence of a Hofmeister series of anions. Despite

the decreased stability of the star polymers in aqueous solution of cosmotropic anions, which would tend to increase adsorption to a surface, the adsorption is still dominated by pH effects that govern the substrate surface charge.

3.1 PEO star brush nanoparticles

3.1.1 Star polymer characterization

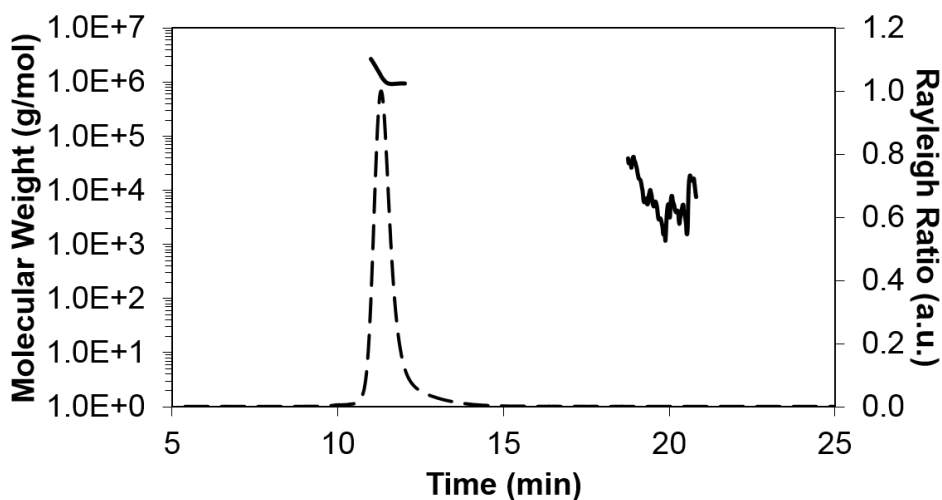


Figure 3.1. SEC-MALLS of star PEO in DI water. The dashed line is the Rayleigh Ratio, or scattered light signal. The solid lines are the absolute molecular weights measured by MALLS.

MALLS (**Figure 3.1**) and dynamic light scattering analysis (**Figure 3.2**) indicated a weight average molecular weight $M_w = 1.2 \times 10^6$ ($M_w/M_n = 1.08$), and intensity-weighted average $R_G = 14 \pm 0.3$ nm and $R_H = 13 \pm 0.5$ nm (number average $R_G = 12 \pm 0.2$ nm and $R_H = 11 \pm 0.4$ nm). The material is 80 wt% PEOMA, so the overall molecular weight of 1.2×10^6 indicates there are approximately 460 PEO arms per star. Although the detailed internal distribution of mass and refractive index in the star polymers is not known, R_G being slightly greater than R_H would indicate these star polymers are not spherical but somewhat elongated, assuming

they behaved as rigid bodies. We interpret the structure of the star polymers using the star-like micelle model of Vagberg and coworkers¹, originally developed to describe the dimensions of block copolymer micelles that have a corona of polymer chains surrounding a core of finite size. The radius of such a particle is predicted as:

$$R_p = \left(\frac{8}{3} \frac{N f^{(1-\nu)2\nu}}{4^{1/\nu} \nu} a^{1/\nu} + R_c^{1/\nu} \right)^\nu \quad (3.1)$$

where R_p and R_c are the radii of the particle and core respectively, $N = 45$ is the number of segments in each arm, $a = 0.36$ nm is the statistical length of an EO segment, $f = 460$ is the number of arms attached to the core, and $\nu = 3/5$ is the Flory exponent for a good solvent. The first term in parentheses in equation 3.1 accounts for the spherical corona of polymer arms and is derived from the blob model of Daoud and Cotton². The second term represents the core. Assuming a dense spherical core composed entirely of pDVB, the core radius is

$$R_c = \left(\frac{3}{4\pi} \frac{M_{pDVB}}{N_A \rho_{pDVB}} \right)^{1/3} \quad (3.2)$$

where $M_{pDVB} = 240\,000$ is the molecular weight of pDVB determined from conversion data, N_A is Avogadro's number, and $\rho_{pDVB} = 1.02$ g/cm³ is the bulk density of pDVB. Equation (2) indicates $R_c = 4.5$ nm. This confirms that the core has a non-negligible size, in keeping with the premise of this model. With this core radius, equation (3.1) predicts $R_p = 14$ nm, consistent with the light scattering measurements. Using the measured R_G and the calculated core radius, the PEO arms in the star polymers have an estimated length $R_{arm} \approx R_G - R_c \approx 8$ nm. This

is compared to the unperturbed root mean squared radius of gyration that the sidechains would have in aqueous solution, given in nm for a PEO chain as³

$$\langle R_g^2 \rangle^{1/2} = 0.445N^{0.58} \quad (3.3)$$

For $N = 45$, this is 4.0 nm. Thus, the polymer arms are estimated to be stretched at a length approximately twice that of free chains.

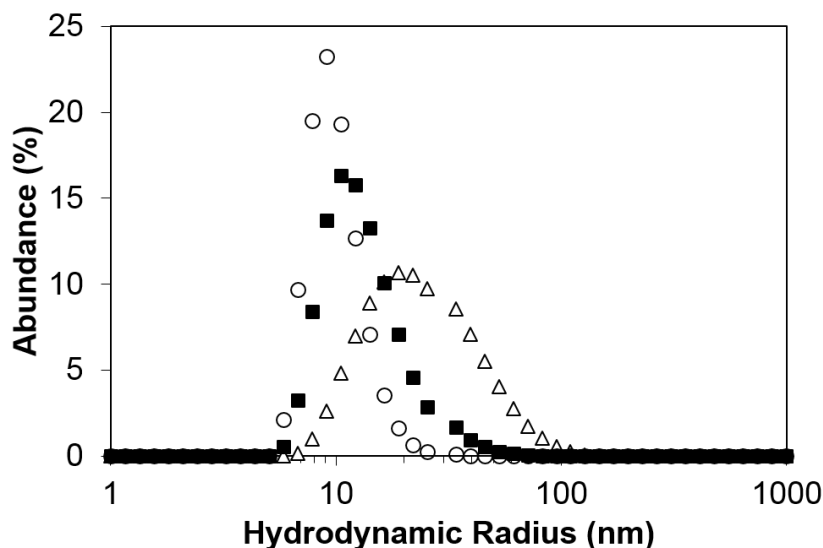


Figure 3.2. Hydrodynamic size distributions of star PEO measured by dynamic light scattering. Number-average (circles, $R_H = 11.6$ nm), volume average (squares, $R_H = 14.1$ nm), and intensity-average (triangles, $R_H = 22.1$ nm). Differences in the distributions are attributed to sample size polydispersity.

3.2 Adsorption of linear and star PEO on silica

3.2.1 Adsorption isotherms on silica

Ellipsometry is used to evaluate the surface excess concentration, or adsorbed amount, of star and linear PEO on silica surfaces. *In-situ* adsorption kinetics for star PEO and 1 MDa molecular weight linear PEO from de-ionized water are shown in **Figure 3.3**. Star PEO achieves an adsorbed mass

approximately 3-4 times higher than the linear PEO at a bulk concentration of 0.01 wt% polymer. Both polymers exhibit similar kinetic behavior; a constant rate of adsorption while the surface is sparsely populated, followed by a slow approach to surface saturation at high surface coverage. The late-time adsorption kinetics for star PEO are plotted versus the inverse square root of time in **Figure 3.3**. The $t^{-1/2}$ kinetics are characteristic of an RSA mechanism⁴, and extrapolation to infinite time yields the jamming limit adsorbed amount. For star PEO, this corresponds to 3.16 mg/m². These results show that true saturation is not achieved over a 2 hour period, and that slow adsorption kinetics can lead to an additional 10-15% adsorbed mass given extended adsorption time. It is not entirely feasible to perform all experiments until the surface is truly saturated, thus all experiments are performed over a 2-6 hour period and the measured surface excess concentration is considered to be the quasi-steady state adsorbed amount.

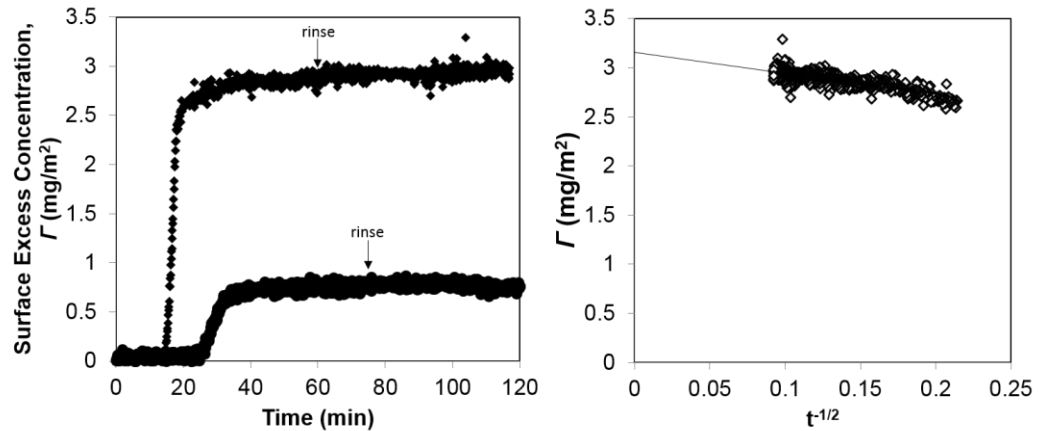


Figure 3.3. Adsorption of linear PEO (circles) and star PEO (diamonds) on silica from 0.01 wt% solutions in de-ionized water, measured by ellipsometry. Bulk solution is rinsed after approximately 40 minutes of adsorption for each layer. *Right:* late-time RSA kinetics of PEO star adsorption, indicating a jamming limit coverage at infinite adsorption time of 3.16 mg/m².

Adsorption isotherms are obtained by measuring the surface excess concentration of star and linear PEO as a function of bulk solution concentration, shown in **Figure 3.4**. Both polymers adsorbed in direct adsorption experiments showed a high affinity adsorption isotherm on silica. Plateau surface excess concentrations reached approximately $2.7 \pm 0.15 \text{ mg/m}^2$ for star PEO, whereas the high molecular weight linear PEO adsorption maximum was approximately $0.7 \pm 0.04 \text{ mg/m}^2$. The latter is consistent with literature values for high molecular weight PEO adsorption to silica.⁵ The PEO arms account for approximately 80 wt% of the star structure, so 2.7 mg/m^2 corresponds to a surface excess concentration of approximately 2.2 mg/m^2 of PEO, which is still three times the amount of PEO adsorption achieved by the linear polymer. This enhancement of PEO adsorption in the form of star polymers is not something that happens with amphiphilic PEO-containing block copolymers on silica in water⁶. PEO star polymer adsorption was also compared to the adsorption that would be displayed by small chains that are comparable in size to the PEO sidechains. Linear 6000 molecular weight PEO was adsorbed to silica in a similar bulk concentration range, but its surface excess

concentration was consistently less than 0.07 mg/m^2 and difficult to distinguish from noise in the ellipsometry signal.

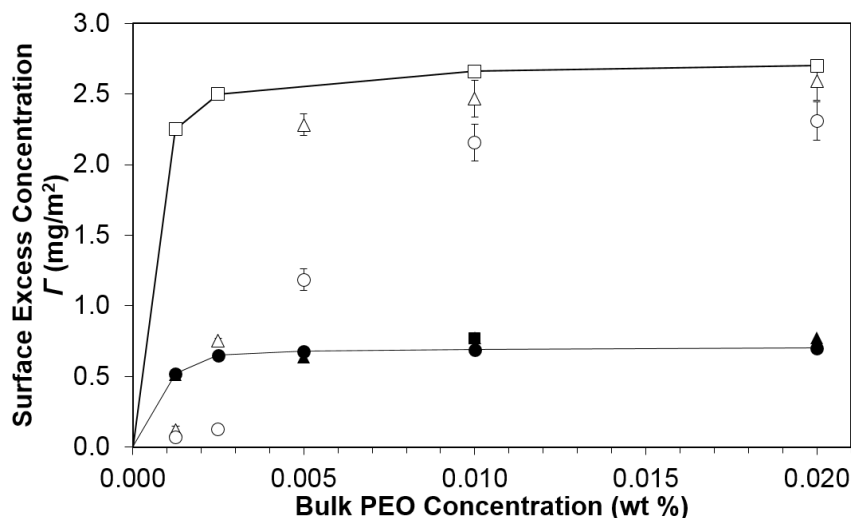


Figure 3.4. Surface excess concentrations of 1.2×10^6 molecular weight PEO star polymers (unfilled symbols) or 1.0×10^6 molecular weight linear PEO (filled symbols) on silica attained via different adsorption procedures: sequential adsorption experiments where 30 minutes ($\circ$ and $\bullet$) or 1 hour (Δ and $\blacktriangle$) were allowed for adsorption after each of several step-wise increases in bulk concentration, or single-shot experiments where polymers adsorbed to an initially bare substrate for 6-10 hours ($\square$ and $\blacksquare$). Lines are drawn to guide the eye.

A previous study by Naderi and coworkers⁷ considered linear PEO bottlebrush polymers that were also based on 2000 molecular weight PEOMA sidechains. These had a molecular weight of 4×10^5 and reached a plateau surface excess concentration of 1.17 mg/m^2 on silica. This falls between the surface concentrations achieved by the linear PEO and the PEO star polymers measured here. The bottlebrush polymer yielded higher surface concentrations than 5×10^5 molecular weight linear PEO in that study, consistent with the current observation of significantly increased adsorption provided by the branched polymer structure. Their PEO bottlebrush layer was significantly denser than the linear PEO layer:

viscous energy dissipation (QCM-D) and steric force measurements showed that the linear PEO layer was actually thicker than the bottlebrush layer. The bottlebrush polymer displayed a steeper, but shorter-ranged steric repulsion between opposing surfaces. The thickness of the linear PEO layer was established by large loop and tail segments, whereas the thickness of the bottlebrush was established mainly by the extension of the low molecular weight PEO sidechains as individual tails protruding into solution.

The observation that PEO star polymers gave still larger surface concentrations than the linear PEO bottlebrush polymers shows that increasing the compactness of the pre-formed PEO brush structure significantly favors denser packing on the surface. The intramolecular cross-links in the star polymer core inhibit its spreading on the surface and allow it to maintain a compact structure that packs mass more efficiently than the bottlebrush polymer.

Examination of the $\sim 2.7 \text{ mg/m}^2$ plateau surface concentration for PEO star polymers in light of the 1.2×10^6 molecular weight and 12 nm number-average R_G :

$$\Theta_{app} = \frac{\Gamma M_w \pi R_g^2}{N_A} \quad (3.4)$$

suggests that approximately 60% of the surface was occupied by PEO stars. This area fraction coverage is sensitive to the star polymer size distribution since these are not monodisperse objects, and it is based on the simple assumption that the stars occupy an excluded area equal to a circle of radius R_G , so the 60% value calculated here should not be over-interpreted. Yet, it is noteworthy that it does somewhat exceed the $\sim 52\%$ jamming limit for random sequential adsorption of low aspect ratio objects.⁸

3.2.2 Effect of pH on PEO/silica adsorption

PEO adsorption on silica in aqueous solution is known to be driven primarily by hydrogen bonding.⁵ Ether oxygen atoms in the PEO backbone are polarized with a partial negative charge, making them hydrogen bond acceptors. Silica surfaces bear hydrogen bond donating silanol (Si-OH) groups in aqueous solution. The percentage of silanol groups that are deprotonated (Si-O⁻) is governed by acid-base equilibrium and the near surface pH.^{9,10} The acid-base and electrical properties of silica surfaces are summarized in **Table 3.1**:

Table 3.1. Properties of the silica/water interface

IEP ^a	pK _{a, app} ^a	ζ^b (mV)	σ (mC/m ²)	σ^c (-e/nm ²)	N _{HB sites} /Star ^d
2.0 – 3.5	7.5	pH 6: -75	pH 6: 7.9	pH 6: 0.05	310
		pH 9: -135	pH 9: 30.2	pH 9: 0.19	250

(a) From reference¹¹; (b) Measured by streaming potential method in 0.01 mM NaCl; (c) Calculated from streaming potential via Gouy-Chapman theory. (d) Estimated from the unperturbed star polymer cross sectional area and a total hydroxyl surface density of 0.5 groups/nm².

Note, the number of available hydrogen bonding sites decreases by approximately 20% by changing the solution from pH 6 to pH 9, based on estimates from surface charge density measurements of the silica/water interface. This highlights the influence of pH on the surface properties of silica and thus the pending adsorption of PEO polymers.

The pH-dependence of linear and star PEO adsorption to silica in de-ionized water (“de-ionized” in the sense that NaOH or HCl are the only intentionally added electrolytes) is shown in **Figure 3.5**. Here, adsorption was

measured by simultaneous ellipsometry/QCM-D. Both linear and star PEO adsorb readily to silica under acidic to neutral conditions. Adsorption becomes reduced around pH 8, and complete prevention of adsorption is achieved at pH 9.2 for linear PEO and 9.5 for star PEO. Both ellipsometry and QCM-D surface excess concentrations reach zero at the pH-induced adsorption cut-off. The prevention of adsorption at high pH is a direct consequence of a reduced population of surface sites available for hydrogen bonding between the polymers and substrate.

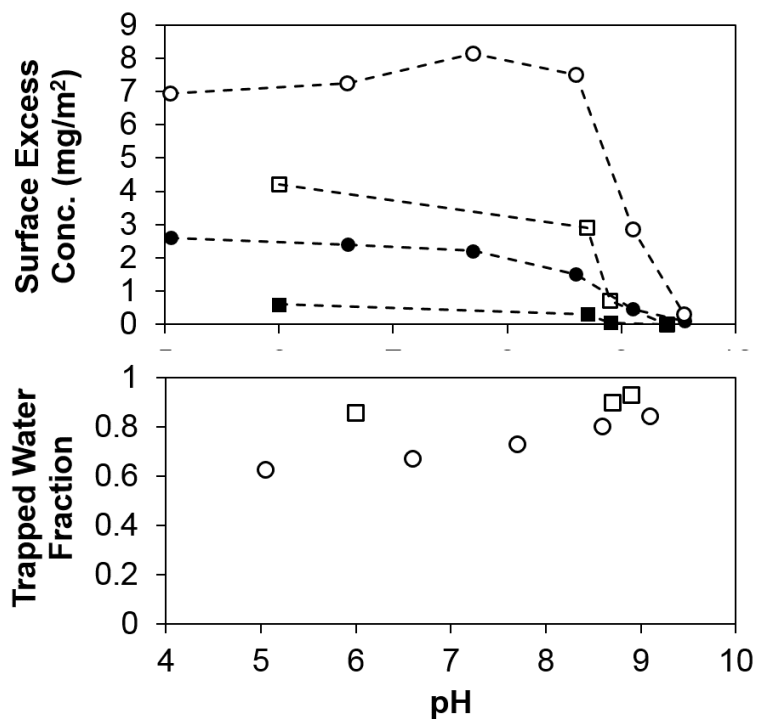


Figure 3.5. Adsorption of linear PEO (1×10^6 Da, squares) and star PEO (circles) measured as a function of pH in 1 mM NaCl by QCM-D (unfilled symbols) and ellipsometry (filled symbols). *Top:* Surface excess concentration, displaying sharp desorption near pH 9. *Bottom:* Trapped water fraction, calculated from the ellipsometry and QCM-D adsorbed amounts: $1 - \Gamma_{\text{ell}}/\Gamma_{\text{qcm}}$.

Ellipsometry purely measures the adsorption of star PEO, and QCM-D includes contributions from both the star PEO and water that is hydrodynamically

coupled with the adsorbed layer during shear oscillation. Combining the adsorbed mass from these two measurements gives an estimate of the fraction of water that is trapped within the layer. **Figure 3.5** also shows a plot of the trapped water content as a function of pH. This analysis shows that star PEO layers consist of a lower fraction of water than the linear PEO. This is expected based on the composition of the star PEO macromolecules and their dense, hydrophobic core. This also suggests a more compact adsorbed layer relative to the linear PEO layer, which will extend in a loop-tail-train conformation that is fully solvated by water.

3.2.3 *Competitive adsorption between linear and star PEO*

Adsorption of polymers to surfaces is well understood to involve a delicate balance between enthalpic gains due to favorable polymer-surface attractions and entropic penalties resulting from reduced configurational degrees of freedom incurred upon confining the polymer to an interface¹². Linear polymers are known to adopt an optimal loop-tail-train conformation at a surface, where trains produce favorable polymer-surface contacts and loops/tails extend away from the interface to minimize entropy loss relative to the polymer's equilibrium bulk solution conformation. The adsorption of branched polymers such as star polymers, bottle-brush polymers, dendrimers, and brush nanoparticles, is governed by the same balance of enthalpy/entropy; however, branched polymers are almost always less conformationally “flexible” than linear polymers due to their macromolecular architecture. This conformational rigidity plays an important role in differentiating the adsorption behavior of highly branched (rigid) polymers and linear (flexible) polymers when adsorbing to an interface. The

earliest studies of branched polymer adsorption was the work of Halperin and Joanny¹³, who theoretically considered the adsorption of a spherical star polymer as a function of its number of arms, length of arms, and polymer-surface attraction strength. Three primary adsorption regimes were established: fully flat star (low arm number), the “sombbrero” with a part of the star flat and part of the star raised (intermediate arm number), and the “droplet” where the star is more-or-less assumes its unperturbed dimensions on the surface. More recently, the phase diagrams have been expanded to star polymers with finite sized cores and charged star polymers¹⁴. One study performed by Striolo and Prausnitz¹⁵ computed the adsorption energy of branched dendrimers and star polymers and compared that energy to the adsorption energy of a linear polymer consisting of the same number of monomers. This study predicts that adsorption is more favorable for linear polymers than branched polymers under strong adsorption conditions, whereas adsorption is more favorable for branched polymers than linear polymers under weak adsorption conditions. These predictions result from differences in the conformational rigidity of the polymers.

Ellipsometry results presented in **Figure 3.6** demonstrate that high molecular weight linear PEO can displace pre-adsorbed PEO star polymers from the silica surface. Competitive adsorption was investigated by allowing either a PEO star polymer layer or a linear PEO layer to reach a steady surface concentration, and then switching to a solution of the other polymer type. When linear PEO was pre-adsorbed and then challenged by a solution of PEO star polymers, there was no detectable change in the ellipsometry signal, and the surface

excess concentration remained constant at 0.7 mg/m^2 for more than an hour of competitive adsorption, despite the fact that PEO star polymers produced three-fold higher surface concentrations than linear PEO in a conventional single-component adsorption experiment. In contrast, when a pre-adsorbed PEO star polymer layer was challenged with a linear PEO solution, the surface excess concentration decreased significantly. Although it had not yet decreased all the way to the 0.7 mg/m^2 surface excess concentration characteristic of linear PEO adsorption, the surface concentration was still decreasing steadily after 80 minutes of linear PEO exposure. Independent experiments were also conducted to measure the degree to which either PEO star polymers or linear PEO desorb during a rinse with polymer-free water. As is normally observed with high molecular weight macromolecules, neither polymer showed any detectable desorption. Thus, since PEO star polymers do not desorb spontaneously, the decrease in surface excess concentration during the competitive adsorption experiment must be due to PEO star displacement by adsorbing linear PEO chains and the formation of a mixed layer.

The results of simultaneous co-adsorption from a mixed solution containing equal concentrations (0.01 wt%) of PEO star polymers and linear PEO were consistent with the competitive adsorption experiments. The adsorption kinetics and final surface excess concentration achieved by co-adsorption were nearly indistinguishable from that formed by linear PEO. The preferential adsorption of linear PEO ensured that the final layer was dominated by the linear polymer.

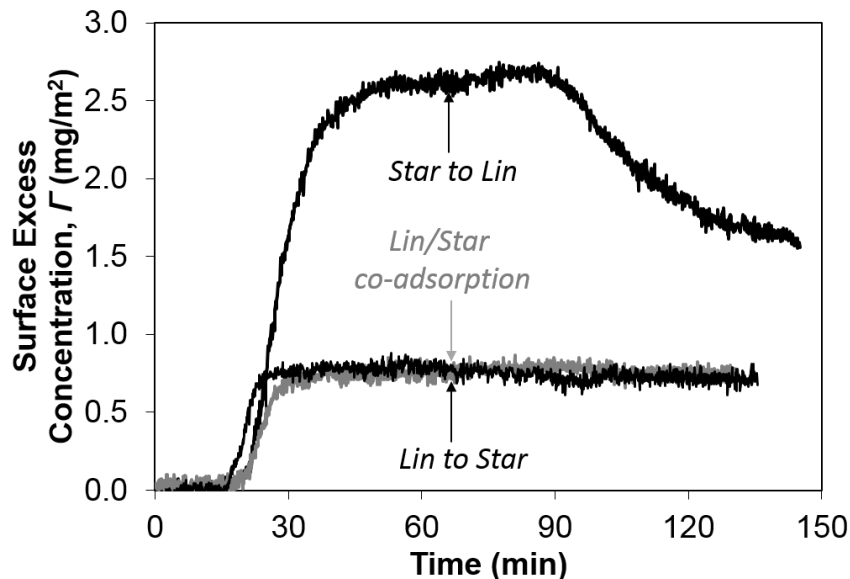


Figure 3.6. *In-situ* competitive adsorption of 1.2×10^6 molecular weight PEO star polymers and 1.0×10^6 molecular weight linear PEO from 0.01 wt% solutions of either polymer. The black (upper) curve illustrates PEO star polymer pre-adsorption followed by switching the solution to linear PEO after 60 min. The grey (lower) curve illustrates linear PEO adsorption followed by switching the solution to PEO star polymer at 60 min. Simultaneous co-adsorption from a solution of 0.01 wt% linear PEO and 0.01 wt% PEO star polymer is shown in black (lower) and overlays the blue curve for linear PEO followed by PEO star polymer.

Competitive adsorption of linear and star PEO at the silica/water interface has also been assessed using quartz crystal microbalance with dissipation (QCM-D). Adsorbed PEO star polymers are challenged by solutions containing linear PEO polymer with molecular weights ranging from 6 kDa to 1000 kDa in order to assess preferential adsorption. The experiments are conducted at pH 5.0 to test surfaces with overall strong adsorption conditions for the PEO/water/silica system. The resulting competitive adsorption measurements are summarized in **Figure 3.7:**

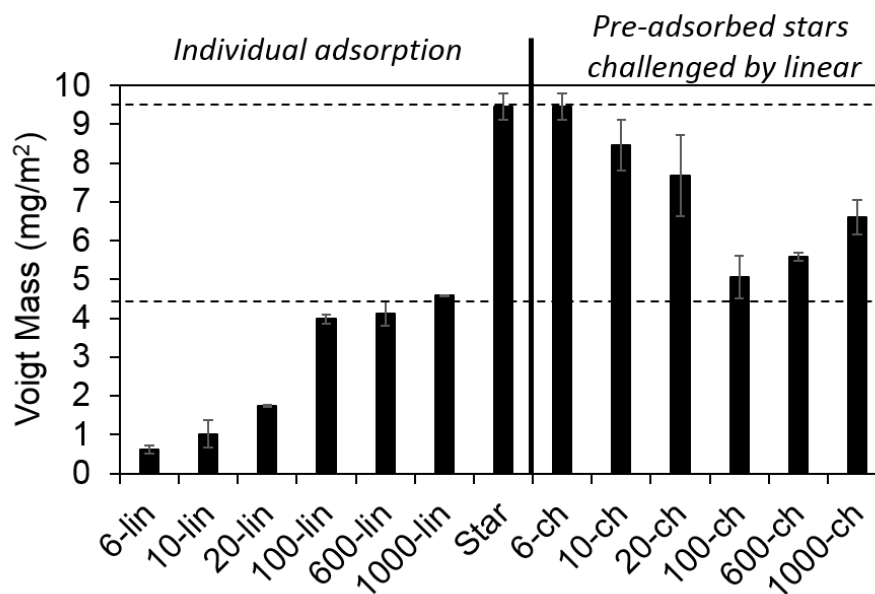


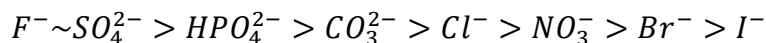
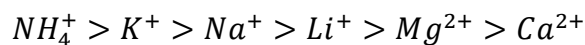
Figure 3.7. Summary of QCM-D measurements of PEO adsorption on silica from de-ionized water, pH 5 – 6. Labels with numbers represent the molecular weight of the linear polymer in kDa. The vertical solid line separates the adsorbed amounts of different species from single-component adsorption on the left from the total adsorbed amounts after competitive adsorption of linear polymer with a pre-adsorbed star polymer layer. The horizontal dashed lines indicate the maximum linear polymer adsorbed amount, 4.5 mg/m², and maximum star PEO adsorbed amount, 9.5 mg/m². The intermediate region is achievable from mixed adsorbed layers.

The displacement of star PEO by linear PEO depends strongly on the molecular weight of the challenging linear PEO polymer. There is little to no displacement of the star polymer by a 6 kDa linear PEO, but displacement does occur for all higher molecular weight linear PEO here from 10 – 1000 kDa. The largest net displacement occurs for 100 kDa linear PEO, near the molecular weight of the 167 kDa star polymers. 600 kDa and 1000 kDa linear PEO still form mixed layers, evident from the adsorbed mass falling between that of the linear polymers and the star polymers produced by single-component adsorption

experiments, however the surface concentration increases with increasing PEO molecular weight about 100 kDa. We cannot distinguish the relative composition of the mixed linear and star polymer layers from just QCM-D measurements, so it is unclear why this increase occurs. It is possible that displacement is constant, but the higher molecular weight polymers replace the displaced stars with more mass.

3.2.4 Hofmeister effects on star PEO stability and adsorption

The Hofmeister series is a scale that ranks the relative effects of ions on the stability of colloids and proteins in aqueous solutions¹⁶. The Hofmeister series exists for both cations and anions, and the orders follows¹⁷ for increased salting out:



The effects are generally much more pronounced for anions than cations. The governing mechanism underlying the strength of Hofmeister effects and the relative order of ions is believed to be the specific interaction between anions and water molecules in the immediate vicinity of the solvated polymer or colloid. It is believed that the ions can strengthen or weaken the strength of hydrogen bonds that occur between the solvating water and the solvated material¹⁸. The result is a strong influence on the enthalpic penalty for displacing the water molecules upon aggregation or adsorption of the material to another surface. Thus, a strongly kosmotropic Hofmeister ion will weaken the hydrogen bond and decrease stability in water, while chaotropic ions strengthen the hydrogen bonds and increase

stability. It is expected through this mechanism that Hofmeister ions could be used to control both star PEO stability in aqueous solution and also the adsorption properties¹⁹, both of which depend primarily on hydrogen bonding interactions.

The stability of star PEO polymers in the presence of Hofmeister anions is assessed by turbidity measurements in **Figure 3.8**. The results are in agreement with previous studies made in our group on star PEO²⁰. PEO exhibits a lower critical solution temperature in water, meaning it becomes less stable as the temperature of the solution is increased. Star PEO is found to flocculate at a temperature of 97 °C in de-ionized water. This is the temperature where a 0.1 wt% star polymer dispersion becomes turbid and strongly scatters light and is referred to as the critical flocculation temperature (CFT). The CFT is measured for star PEO dispersions containing varying amounts of sodium Hofmeister salts. Sodium thiocyanate (SCN^-), sodium chloride (Cl^-), sodium carbonate (CO_3^{2-}), and sodium phosphate (PO_4^{3-}) are used to span the Hofmeister series. The thiocyanate ion is considered a chaotropic anion, and chloride, carbonate, and phosphates being kosmotropic anions. The kosmotropic anions follow the order in terms of strength of de-stabilization, $\text{Cl}^- < \text{CO}_3^{2-} < \text{PO}_4^{3-}$. The CFT is shown to increase slightly upon the addition of thiocyanate, indicating its chaotropic influence on the stability of star PEO. The effects of kosmotropic anions follow the expected Hofmeister series, with the CFT decreasing for all three anionic species. Carbonate and phosphate are shown to decrease the CFT to within 5 °C of room temperature upon the addition of 500 mM and 325 mM salt, respectively. The linear decrease in CFT with added salt has been observed similarly for other ethoxy- and

propyloxy-ethylene based polymers and various Hofmeister anions²¹. The turbidity measurements indicate that the solvent quality can be effectively controlled through the addition of Hofmeister anions. This effect has been utilized toward driving adsorption of thermoresponsive polymers to a surface by initiating adsorption at temperature below, but approaching, the CFT of the polymer²². The enhancement of polymer-surface interaction would be favorable for forming densely-packed layers of brush nanoparticles.

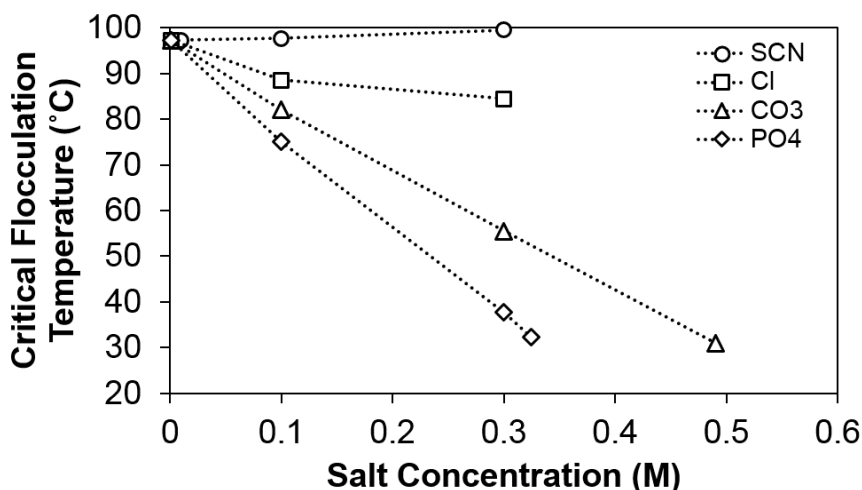


Figure 3.8. Thermally responsive aggregation of star PEO in the presence of various Hofmeister anions (from sodium salts). The decrease in CFT corresponds with the relative kosmotropic strength of the anion.

The adsorption of star and linear PEO in the presence of the aforementioned Hofmeister anions were measured by QCM-D as shown in **Figure 3.9**. The surface excess concentration is plotted first against salt concentration for chloride, thiocyanate, and carbonate ions. Measurements were made with phosphate ions present, but no adsorption occurs in the presence of phosphate. The adsorbed mass of the linear and star PEO are also measured in de-

ionized water as a reference. In DI water, linear PEO achieves a total adsorbed mass (polymer + trapped water) of 5.5 mg/m^2 and star PEO reaches 9.0 mg/m^2 . This is consistent with previous observations in this chapter. The adsorbed mass increases for star PEO upon the addition of 10, 100, and 300 mM NaCl, and a small increase is observed for linear PEO at the same salt concentrations. Increased adsorption is also measured for the addition of 10 and 300 mM NaSCN. Interestingly, the addition of dilute Na_2CO_3 (0.01 – 0.1 mM) completely prevents adsorption of linear PEO and reduces the adsorbed amount of star PEO. The mechanism for this is made more apparent when the same data is plotted against the bulk solution pH, measured from independently prepared solutions. The effect of pH clearly plays a prominent role in governing adsorption, and a similar trend of a pH-induced adsorption cutoff is observed for carbonate solutions that was observed earlier by addition of hydroxide to deliberately increase pH. This is an example of surface limitations prevailing over decreased solvent quality effects. Interestingly, star PEO remains adsorbed under salt conditions where linear PEO does not. This is possibly attributed to differences in the entropy penalty for adsorption to the surface¹⁵.

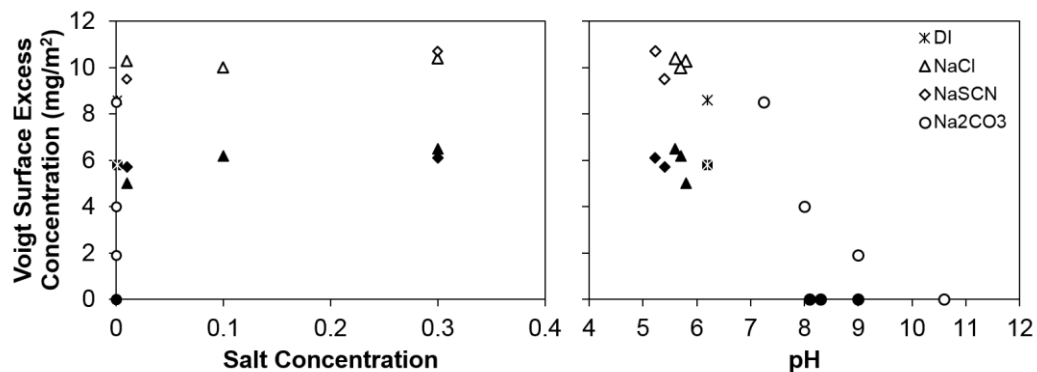


Figure 3.9. Adsorbed amount measured by QCM-D for star PEO in salt solutions containing sodium salts of Hofmeister anions. Unfilled symbols are star PEO and filled symbols are linear PEO. *Left:* Voigt mass versus salt concentration. The low salt values are for sodium carbonate solutions, and are $\sim 10^{-5} - 10^{-4}$ M. *Right:* Same adsorption data, plotted against the corresponding bulk solution pH.

3.3 Conclusions

We have characterized the adsorption of a novel core-crosslinked PEO based star copolymer on silica surfaces. The adsorption of star PEO is compared throughout to the adsorption of a high molecular weight linear PEO polymer to highlight the differences in adsorbed layer structure and properties resulting from a compact, star polymer architecture. Adsorption isotherms are measured using ellipsometry, where star PEO adsorbs to significantly higher surface excess concentrations than linear PEO chains of an equally large molecular weight. The saturation surface concentration for the PEO star polymers is approximately three times greater than it is for the comparable linear PEO. The compact star polymers pack efficiently on the surface and provide a route to establishing very dense layers with a large number of chain ends oriented toward solution. Such layers may be expected to be effective agents for steric stabilization or boundary lubrication. Despite the high packing efficiency, elasticity constraints affect the strength of PEO

star adsorption in competitive adsorption situations. PEO star polymers can be displaced from the interface by linear PEO, suggesting that care would need to be taken when formulating a multi-component stabilizing or lubricating system in order to decrease the likelihood of star polymer displacement from the surface.

The influence of pH on adsorption in the PEO/silica/water system was also investigated. Adsorption here is mediated by hydrogen-bonding between EO units in the polymer and surface silanol groups. The density of silanols can be varied on the surface using pH to shift local acid-base conditions. A sharp desorption threshold is found to occur between pH 9.0 – 9.5 for both linear and star PEO due to de-protonation of the silanol groups and a net reduction in the enthalpic gains realized on adsorption, but there was a small difference in the pH cutoff for star and linear PEO. Star PEO remained adsorbed at a slightly higher pH, thus slightly weaker adsorption strength, than linear PEO, consistent with the reduced entropic penalty for adsorption of the compact star polymers relative to the linear polymers.

Attempts at utilizing a Hofmeister series to probe the strength of the hydrogen bond interactions were made, but ultimately adsorption remained governed by pH and less so by specific ion effects. Preferential adsorption of star PEO over linear PEO under weak adsorption conditions highlights the importance of both entropic and enthalpic interactions in differentiating the adsorption of multichain star and linear polymers.

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4. Stimuli-responsive swelling and adsorption of polyelectrolyte brush-grafted nanoparticles

This chapter presents a study of pH, ionic strength, and temperature effects on the free suspension and interfacial adsorbed layer properties of SiO₂-*g*-PDMAEMA brush-grafted nanoparticles. PDMAEMA is a pH- and thermally-responsive polymer exhibiting a lower critical solution temperature (LCST) in aqueous solution. The LCST depends strongly on the degree of protonation of tertiary amine groups on each monomer, and the degree of protonation is governed by acid-base equilibrium and local pH conditions. PDMAEMA retains its pH and thermal responsiveness when tethered to a surface in a brush conformation, thus SiO₂-*g*-PDMAEMA nanoparticles exhibit colloidal properties that respond to changes in aqueous solution temperature and ionic composition. These factors dictate how mutually repellant BGNPs will pack on an electrostatically attractive surface. This chapter identifies a broad range of conditions that can be used to form sub-monolayer, spatially-heterogeneous SiO₂-*g*-PDMAEMA adsorbed layers. Effective surface coverages between $\sim 1 - 75\%$ can be achieved depending on the adsorption conditions and particle properties. Hysteretic adsorption effects are investigated, and these are used to engineer SiO₂-*g*-PDMAEMA layers in ways that can be leveraged to control surface forces in subsequent chapters.

4.1 SiO₂-*g*-PDMAEMA nanoparticles

SiO₂-*g*-PDMAEMA have a 20 nm silica nanoparticle core surrounded by a PDMAEMA brush with grafting density $\sigma = 0.46$ chains/nm², arm-average

molecular weight $M_n = 22\,870$ (degree of polymerization $N \sim 145$), and polydispersity index $PDI = 1.13$. SiO_2 -*g*-PDMAEMA is synthesized and characterized as previously published in our group¹. The mass per SiO_2 -*g*-PDMAEMA nanoparticle is calculated from the sum of the particle and polymer masses as:

$$m_{core} = \frac{4}{3}\pi R_{core}^3 \rho_{SiO_2} \quad , \quad m_{brush} = \frac{4\pi R_{core}^2 \sigma M_w}{N_A}$$

The calculated mass per particle is used to convert surface excess concentration or adsorbed mass, measured by ellipsometry, into a number density of adsorbed particles for estimations of surface coverage.

4.1.1 Particle size and charge

The pH dependence of the SiO_2 -*g*-PDMAEMA hydrodynamic radius in 1, 10, and 100 mM NaCl solutions is shown in **Figure 4.1**. The lower limit for the particle size is restricted by the SiO_2 nanoparticle core radius $R_c = 10 \pm 2$ nm, and the upper limit is estimated as the core radius plus the PDMAEMA contour length $L_0 = n_{DMAEMA} a_{DMAEMA} = 36$ nm for $n_{DMAEMA} = 145$ and repeat unit length $a_{DMAEMA} = 0.25$ nm. The degree of protonation of the weak base DMAEMA repeat units in the brush, α , is determined by pH and ionic strength, and this in turn controls the brush swelling. The measured R_h decreased with increasing pH for all NaCl concentrations due to DMAEMA deprotonation. Brush collapse was sharpest at pH $\sim 7 - 8$, around the PDMAEMA pK_a of 7.0-7.5 reported in the literature.^{2,3}

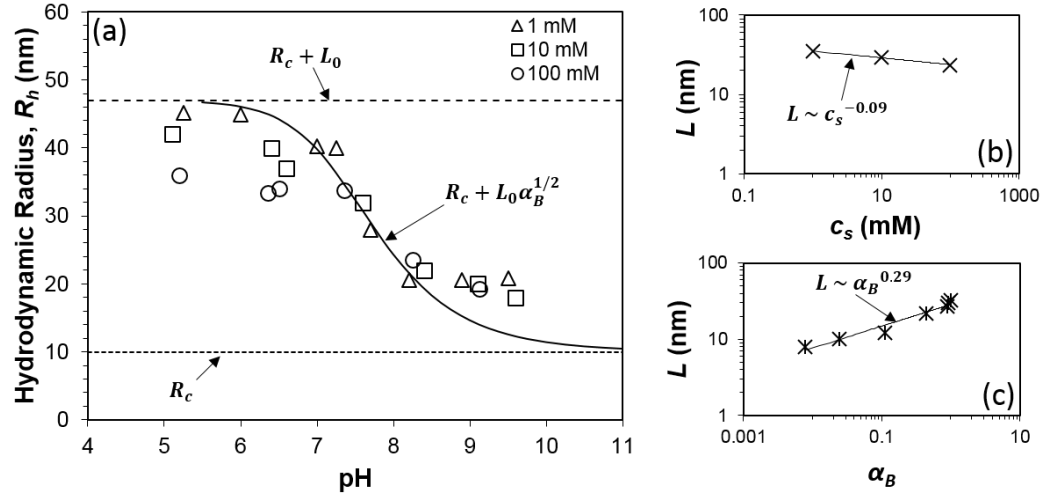


Figure 4.1. (a) Number average hydrodynamic radius of SiO₂-g-PDMAEMA nanoparticles in aqueous NaCl solutions measured by DLS: (Δ) 1 mM, ($\square$) 10 mM, ($\circ$) 100 mM NaCl. The curve shows the osmotic brush prediction. (b) Ionic strength effects on brush thickness L at pH 6 ($\alpha_B \approx 0.97$), with power law fit. (c) Effect of increasing ionization (decreasing pH) on L in 10 mM NaCl, with power law fit.

In a study of pH-dependent block copolymer micelles with PDMAEMA coronas, Lee and co-workers⁴ formulated a star-like micelle model utilizing electrostatic blobs to describe the micelle size as $R_p = R_c + L_0 \alpha_B^{1/2}$, where α_B is the degree of ionization that would be expected for individual PDMAEMA chains in bulk solution. This has the same $\alpha_B^{1/2}$ scaling as the original theory of osmotic polyelectrolyte brushes developed by Pincus.⁵ The experiments in Figure 1 were conducted in 1-100 mM NaCl and are thus not in the osmotic brush regime. Nevertheless, **Figure 4.1** shows that the star-like micelle model is reasonably consistent with the measured swelling dependence on pH. At high pH where the brush was only weakly charged, its thickness became independent of ionic strength, and at pH > 8.5, the thickness of the brush, estimated simply

as $L = R_h - R_c$, remained constant at approximately 10 nm for each ionic strength. Figure 4.1b shows the estimated brush thickness as a function of ionic strength at pH 6 when the brush was highly charged. Increased charge screening decreased the brush thickness with increasing salt concentration C_s , scaling as $L \sim C_s^{-0.09 \pm 0.01}$. This dependence is somewhat weaker than predicted by Zhulina and Borisov for spherical, annealed polyelectrolyte brushes⁶ where

$$L \sim N^{3/5} f^{1/5} \alpha^{2/5} (C_s l^3)^{-1/5} l \quad (4.1)$$

with f the number of chains, N the number of statistical segments, and l the statistical segment length. The data are consistent with the $L \sim C_s^{-0.1}$ scaling predicted by Hariharan and co-workers⁷ based on a blob model of highly curved polyelectrolyte brushes.

Figure 4.1 shows that the brush thickness scaled with the PDMAEMA degree of protonation as $L \sim \alpha_B^{0.29 \pm 0.06}$, again assuming the degree of protonation expected of isolated chains in solution, α_B . The scaling was nearly identical for 1 mM and 100 mM NaCl (not shown), with power-law exponents of 0.28 and 0.27 respectively. Neutron scattering measurements from aqueous PDMAEMA solutions⁴ have shown that the segment length scales with fractional charge as $l \sim \alpha_B^{0.2}$. By the condition that $Nl = L_0 = \text{constant}$, N must scale oppositely to the segment length as $N \sim \alpha_B^{-0.2}$. Inserting these scaling relations into equation (1) predicts $L \sim \alpha_B^{0.36}$, in reasonable agreement with the data.

Swelling and collapse of the SiO₂-*g*-PDMAEMA BGNPs in bulk suspension was completely reversible. When the pH of a 1 mM NaCl dispersion was cycled back and forth four times between pH 5 and 9 over the course of 1 h,

the hydrodynamic radii were consistently found to be $R_h(pH\ 5) = 45.6 \pm 1.7\text{ nm}$ and $R_h(pH\ 9) = 18.9 \pm 0.7\text{ nm}$.

The pH dependence of the apparent zeta potential of SiO_2 -*g*-PDMAEMA particles is shown in **Figure 4.2**. The electrophoretic mobility decreased with increasing pH due to brush deprotonation as expected and exhibited an isoelectric point near pH 9.3 for each ionic strength. The slight negative charge at high pH is attributed to ungrafted silanol groups on the silica core. The influence of pH on the apparent zeta potential was qualitatively similar to its effect on BGNP size. Increasing $\zeta_{p,app}$ correlated directly with increasing R_h for all three salt concentrations, illustrating the link between intra-brush electrostatic interactions and brush swelling.

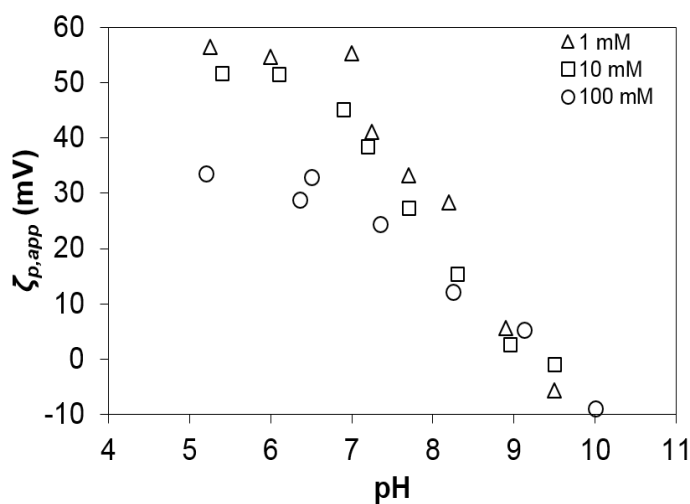


Figure 4.2. Apparent zeta potential of 0.1 mg/mL SiO_2 -*g*-PDMAEMA suspension in NaCl solutions as a function of pH for (Δ) 1 mM; (□) 10 mM; (○) 100 mM NaCl.

Note that in the case of a polyelectrolyte brush-grafted nanoparticle, $\zeta_{p,app}$ calculated from electrophoretic mobility using the Henry equation is not equal to

the zeta potential defined as the potential at the surface of shear adjacent to the particle. The difference is due to the three-dimensional distribution of charge throughout a brush that has a significant thickness relative to the Debye length as well as the hydrodynamic effect of the brush itself on fluid flow around the particle. Electrophoresis of polymer-coated particles (“soft colloids”) is discussed in detail by Oshima⁸ and by Hill and co-workers.^{9,10} Implementation of the soft-particle electrokinetic model of Hill and co-workers to the current BGNP system results in electrical potentials at the outermost edge of the brush as high as +115 mV in 1 mM NaCl due to the high grafting density and large number of ionizable units in the brush. For convenience $\zeta_{p,app}$ is used in the remainder of this work to interpret trends in adsorption behavior.

4.1.2 Critical flocculation temperature

Figure 4.3 shows the pH and ionic strength dependence of SiO₂-*g*-PDMAEMA flocculation in aqueous NaCl solutions. The CFT was measured for $\sigma = 0.22$ chain/nm², $M_n = 25,000$ and $\sigma = 0.46$ chain/nm², $M_n = 21,870$ brush-grafted nanoparticles in 1 mM and 10 mM NaCl. The CFT is found to depend most strongly on the solution pH and the degree of protonation of the particles. The CFT varies from approximately 90 - 105 °C when the particles are strongly charged at pH 5 - 7, then gradually decreases near the pK_a in the pH range 7 - 8, and finally plateaus to approximately 40 – 50 °C when the particles are uncharged at pH 8.5 - 10. This trend is indicative of two simultaneous phenomena: 1) the decreasing solvent quality of individual PDMAEMA chains in the brush, leading to increasingly attractive polymer-polymer interactions, and 2) decreasing

colloidal stability due to decreased electrostatic and electrosteric repulsions as the particle charge and brush length are reduced. The combination of changes in local polymer-solvent interaction energy and particle-particle brush stabilization forces leads to the broad range of temperature sensitivity.

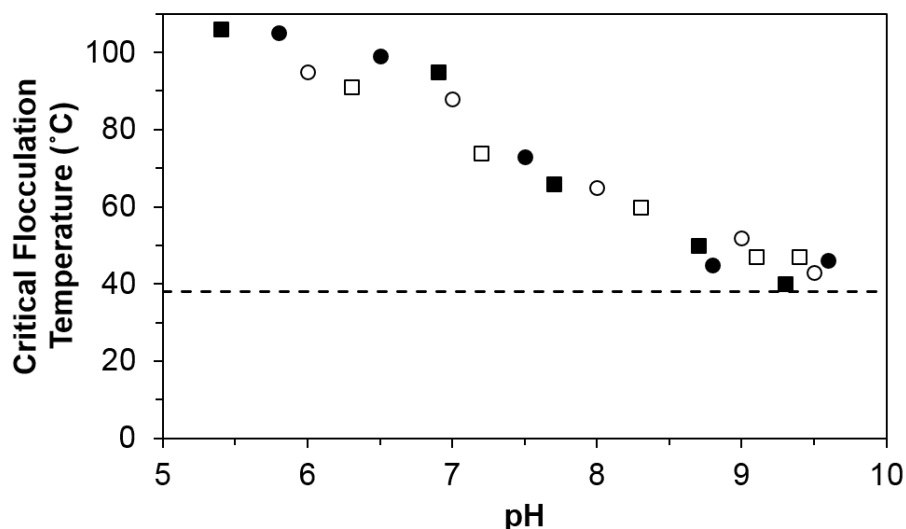


Figure 4.3. Critical flocculation temperature for 1.0 mg/mL dispersions of SiO₂-*g*-PDMAEMA as a function of pH and ionic strength. Unfilled symbols are 1 mM NaCl and filled symbols are 10 mM NaCl, for $\sigma = 0.22$ chain/nm², $M_n = 25,000$ (circles) and $\sigma = 0.46$ chain/nm², $M_n = 21,870$ (squares). Thermal responsiveness can be achieved over a 70 °C window.

4.2 Electrostatic adsorption to silica substrates

4.2.1 Ellipsometry

Linear PDMAEMA adsorption to the silica/water interface has been studied in detail by the Santore group, who found its adsorption to be driven purely by electrostatics^{11,12}. Accordingly, a sharp adsorption cutoff was observed at high pH with moderate to high ionic strengths due to the absence of any strong non-electrostatic attraction to the surface. We measured linear PDMAEMA ($M_w =$

56,000. PDI = 1.18) adsorption to the silica/water interface at a concentration of 100 ppm as a function of pH and NaCl concentration using ellipsometry. The results are presented in **Figure 4.4**. At low pH, a high percentage of charged repeat units results in strong attraction to the surface. This is compensated by the strong intra- and inter-chain electrostatic repulsions that result in a relatively low surface excess concentration of $\Gamma = 0.6 - 0.7 \text{ mg/m}^2$, independent of salt concentration, at pH 7 and below.

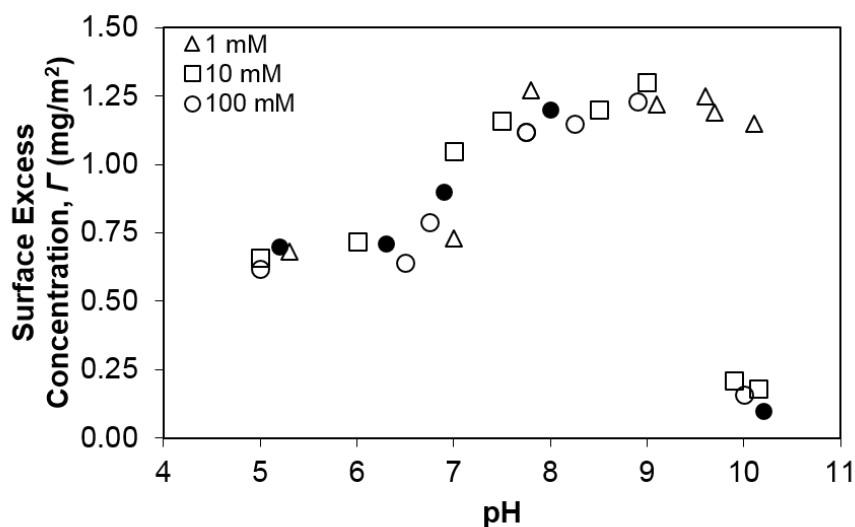


Figure 4.4. Adsorption of linear PDMAEMA at 0.1 mg/mL to the silica/aqueous interface measured by ellipsometry in the presence of (Δ) 1 mM; ($\square$) 10 mM; ($\circ$) 100 mM NaCl. Filled symbols are direct adsorption and unfilled symbols are sequential adsorption measurements. Little to no hysteresis is observed.

As pH was increased and repeat units became increasingly deprotonated, the surface excess concentration increased when approaching the pK_a . This behavior is well established for electrostatic adsorption of linear polyelectrolytes,¹³ not only because of the decrease in lateral electrostatic repulsion, but also because the decreasing polyelectrolyte charge density allows

an increasing fraction of segments in loops or tails,¹⁴ compared to the mostly train conformation typical of adsorbed, high linear charge density polyelectrolytes. A broad maximum in surface concentration of 1.2 – 1.4 mg/m² was established near pH 9. The surface excess concentration decreased as the pH was further increased to 10, where less than 1% of repeat units were charged. The surface excess concentration decreased only slightly in 1 mM NaCl solution, but it decreased nearly ten-fold in 10 and 100 mM NaCl. A small amount of linear PDMAEMA adsorption at high pH is likely due to residual protonated monomers or to induced protonation in proximity to the negatively charged surface. The linear polymer behavior at high pH was consistent with the sharp adsorption cutoff reported previously for higher ionic strength solutions.

The final issue of note with respect to linear PDMAEMA adsorption is that its adsorption was reversible with respect to pH changes. The filled symbols in **Figure 4.4** are representative of *direct adsorption* of PDMAEMA to a bare surface. The unfilled circles show *sequential adsorption* experiments where PDMAEMA was adsorbed, then followed by changes in pH at random. Those surface excess concentrations were in good agreement with the direct adsorption measurements, indicating reversible adsorption with respect to pH variation for the linear PDMAEMA.

Adsorption of SiO₂-*g*-PDMAEMA (grafting density: 0.46) directly to bare silica at a 100 ppm concentration is shown in **Figure 4.5**. At lower pH (5-8), the surface excess concentration increased approximately linearly with increasing pH. This behavior occurred at all three ionic strengths, with higher ionic strength

yielding higher surface excess concentration. In the range pH 5-8, the surface excess concentration increased from ~ 0.5 to $\sim 0.8 \text{ mg/m}^2$ in 1 mM NaCl and from ~ 0.5 to $\sim 1.7 \text{ mg/m}^2$ in 100 mM NaCl. pH increases decrease charge in the grafted brushes and increasing salt concentration enhances charge screening. Both effectively decrease the strength of the lateral electrostatic repulsions between particles, enabling closer particle packing at the interface. At approximately pH 8 the surface excess concentration began to increase strongly for 1 and 10 mM NaCl, reaching a sharp adsorption maximum around pH 9.

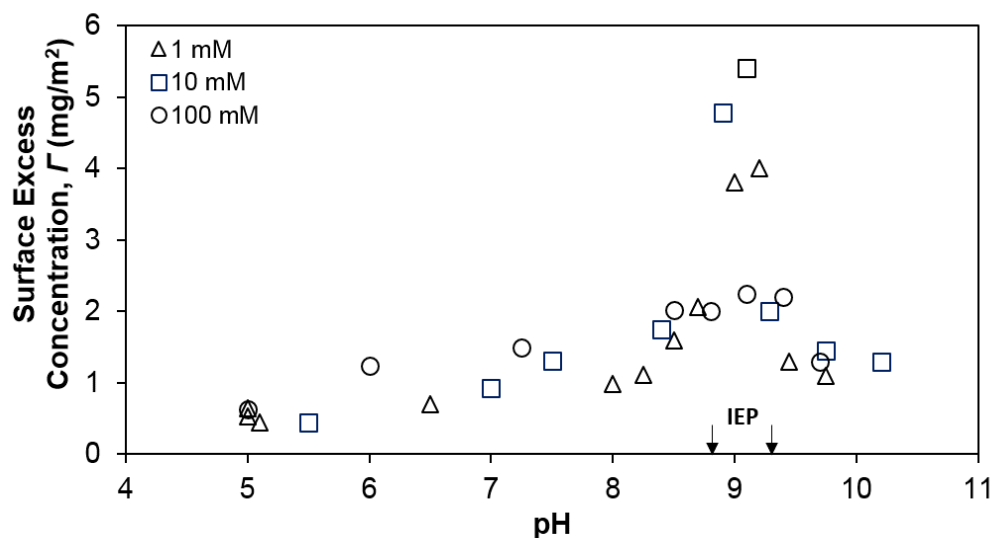


Figure 4.5. Direct adsorption of $\text{SiO}_2\text{-g-PDMAEMA}$ at 100 ppm to the silica/aqueous interface measured by ellipsometry. Surface excess concentration as a function of pH for particles in (Δ) 1 mM; ($\square$) 10 mM; ($\circ$) 100 mM NaCl. Arrows indicate the range of isoelectric points of the particles at different ionic strengths. Maximum packing of particles is found in this range.

The extent of adsorption is maximal near the isoelectric point because it is here that lateral electrostatic repulsions are minimized, provided there is a residual attraction to the surface. Electrophoretic mobility measurements (Figure 4.2) indicated an isoelectric point of $\text{pH } 9.1 \pm 0.2$ for $\text{SiO}_2\text{-g-PDMAEMA}$, matching

the pH for maximum adsorption. The maximum surface excess concentration was sensitive to ionic strength, reaching $4.0 \pm 0.3 \text{ mg/m}^2$ for 1 mM and $5.4 \pm 0.4 \text{ mg/m}^2$ for 10 mM NaCl solutions. A sharp pH adsorption maximum was not observed for 100 mM NaCl, indicating the existence of an ionic strength adsorption maximum somewhere between 1 and 100 mM at pH 9. The optimum ionic strength was not pursued.

Above pH 9, the surface excess concentration decreased to the 1 – 2 mg/m^2 range as the electrostatic attraction to the surface further weakened, and the net charge on the particles had become slightly negative. The latter would produce finite lateral electrostatic repulsions that were absent at the isoelectric point. Adsorption despite having the same net sign of charge as the surface suggests that DMAEMA protonation is promoted by close proximity to the charged surface. Retention of significant adsorption at high pH distinguishes the SiO_2 -*g*-PDMAEMA from linear PDMAEMA. A small fraction of protonated DMAEMA units in the large number of grafted chains evidently provides sufficient electrostatic attraction to drive adsorption, even for the 10 and 100 mM NaCl conditions where the extent of linear polymer adsorption was more severely decreased. The difference between SiO_2 -*g*-PDMAEMA and linear PDMAEMA at high pH will be shown below to be even more pronounced in sequential adsorption experiments.

The persistence of adsorption for SiO_2 -*g*-PDMAEMA BGNPs under weak adsorption strength conditions at elevated pH, where linear PDMAEMA adsorption was nearly eliminated, is attributed to a difference in the entropy of

adsorption for the BGNP and the linear polymer. Simulations by Striolo and Prausnitz¹⁵ revealed similar differences between multi-arm star polymers and linear polymers under weak adsorption strength conditions. Intramolecular crowding in the star polymer inhibits conformational changes of individual chains (“arms”) as the star polymers adsorb. The result is that star polymers experience significantly less loss of configurational entropy upon adsorption compared to linear polymers. Thus, a star polymer, and we argue by analogy a BGNP, can have an overall favorable free energy of adsorption with just a weakly favorable enthalpy of adsorption that would not allow linear polymer adsorption. Just a few charged segments in each of the hundreds of grafted chains in the SiO₂-*g*-PDMAEMA provide enough total charge to adsorb the BGNP via multi-chain contact with the surface.

An increase in pH changes the SiO₂-*g*-PDMAEMA BGNPs in ways that produce opposing effects on adsorption. The decreased charge weakens the attraction to the surface but also weakens the lateral repulsions at the interface. Although the surface attraction is weakened, as long as it is sufficiently strong to allow adsorption, the extent of adsorption will be limited by packing considerations. The weakened lateral repulsions favor closer packing. Furthermore, the brush de-swelling that occurs at higher pH also favors closer particle packing. With a smaller excluded area, more particles can pack in the same area to produce a higher surface excess concentration, as observed near pH 9 in **Figure 4.5**.

4.2.2 QCM-D

Direct adsorption of SiO₂-*g*-PDMAEMA is also assessed by independent QCM-D measurements in **Figure 4.6**. The measured frequency and dissipation shifts exhibit the same characteristic adsorption behavior as displayed in ellipsometry measurements in **Figure 4.5**: small adsorbed amounts at low to intermediate pH, a sharp pH-induced maximum near the particle isoelectric point, followed by a decrease in the adsorbed amount due to reduced particle-surface attraction. Difficulty exists in modeling QCM-D data for SiO₂-*g*-PDMAEMA adsorption due to the heterogeneity of the adsorbed layers and additional energy dissipation mechanisms (*e.g.*, particle rocking¹⁶) that extend past purely viscoelastic film contributions. There is no suitable model to interpret the data quantitatively, but the raw data supports the adsorption mechanism proposed based on ellipsometry measurements.

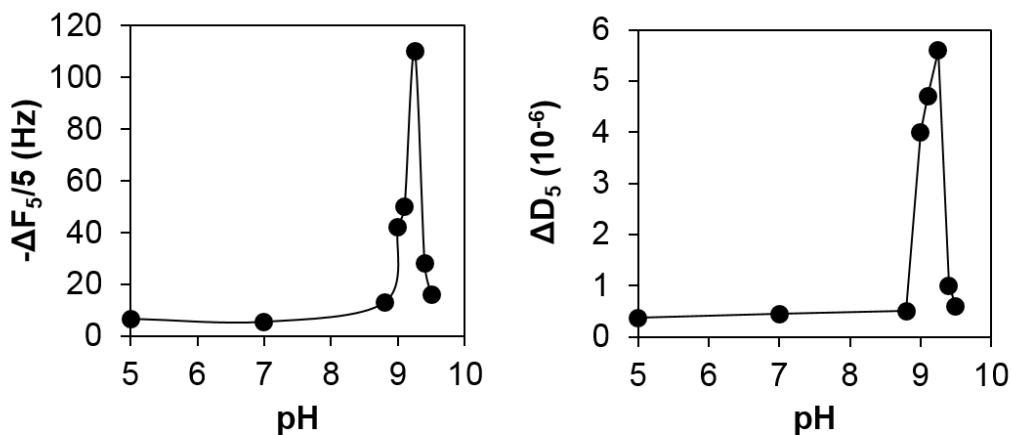


Figure 4.6. Direct adsorption of SiO₂-*g*-PDMAEMA at 100 ppm to the silica/aqueous interface measured by QCM-D. Frequency and dissipation shifts for the fifth overtone number are shown as a function of pH in 10 mM NaCl.

4.2.3 *Electrostatic random sequential adsorption mechanism*

The adsorption behavior of SiO₂-*g*-PDMAEMA can be captured qualitatively using a simplified scaling approach developed by Oberholzer and coworkers as a part of their full-scale electrostatic RSA analysis.¹⁷ The approximate theory considers the effect of long-range electrostatic repulsions between rigid charged spheres as they undergo random sequential adsorption to an attractive surface. The spheres occupy a projected area defined by their radius R , but electrostatic repulsions create a larger excluded area defined by radius R_{ex} . This extended exclusion radius mimics the role of the hard-sphere excluded radius in conventional random sequential adsorption theory for uncharged rigid spheres.¹⁸ Our objective is to interpret trends in the adsorption of SiO₂-*g*-PDMAEMA using the basic concepts of electrostatic RSA. The model is developed for rigid spheres, not soft spheres, but the basic ideas concerning the importance of long-range electrostatic repulsions are informative. The Yukawa potential is used to estimate the ratio R_{ex}/R from the strength of particle-particle repulsions at the surface:

$$U_c = \frac{\bar{N}B_{pp}}{2\left(\frac{R_{ex}}{R}\right)} e^{-2\kappa R[(R_{ex}/R)-1]} \quad (4.2)$$

where U_c is the maximum allowable energy penalty for inter-particle interaction that prevents additional adsorption, $\bar{N}$ is the number of nearest neighbors, and B_{pp} is the Yukawa coefficient for particle-particle electrostatic repulsions:

$$B_{pp} = \left(\frac{4\pi k_B T \epsilon \epsilon_0 R}{e^2}\right) \left(4\gamma + \frac{2}{\kappa R} \gamma^3\right)^2 \quad (4.3)$$

Here, $\gamma = \tanh(\tilde{\psi}_p/4)$ and $\tilde{\psi}_p = \psi_p e/k_B T$ is the dimensionless particle surface potential. For the purpose of interpreting trends in the adsorption of SiO₂-*g*-PDMAEMA with respect to pH changes, we emphasize the basic ideas concerning the importance of long-range electrostatic repulsion among soft charged spheres using electrostatic RSA. The original model was strictly developed for rigid charged spheres. We used dynamic light scattering results to set $R = R_h$ and electrophoretic mobility measurements to approximate the surface potential by equating $\psi_p = \zeta_{p,app}$ to calculate B_{pp} . Unlike the rigid spheres treated by the original model, both the potential and the size are pH dependent for SiO₂-*g*-PDMAEMA. Following Oberholzer and coworkers, we assume $\bar{N} = 6$ nearest neighbors and a reasonable estimate of the adsorption barrier $U_c = 1 k_B T$ in order to estimate R_{ex}/R at each pH using equations (2 and 3). The area fraction surface coverage by charged spheres at the jamming limit is predicted relative to the neutral hard sphere RSA jamming limit θ_{hd} as

$$\theta_{E-RSA} = \theta_{hd} \left(\frac{R}{R_{ex}} \right)^2 \quad (4.4)$$

Simulations with uncharged rigid spheres indicate that $\theta_{hd} = 0.547$. Once the electrostatic RSA jamming limit is calculated, the surface excess concentration is calculated using the BGNP mass and its measured size. Surface excess concentrations estimated in this manner are plotted in **Figure 4.7** for 1 mM NaCl. The particle-particle and particle-surface interaction energies are also shown as a function of pH to demonstrate the interplay of these two electrostatic driving forces. Comparing the predictions of E-RSA in **Figure 4.7** and the experimental

measurements of surface excess concentration via ellipsometry in **Figure 4.5** shows excellent qualitative agreement and captures all relevant features including the sharp adsorption maximum. E-RSA does predict approximately 2 times higher adsorbed amounts than were measured at pH 5, but still is consistent with the picture of a particle-particle repulsion limited adsorption regime while the zeta potential is high. We should mention that the choice of adsorption penalty is arbitrarily set at 1 kT .

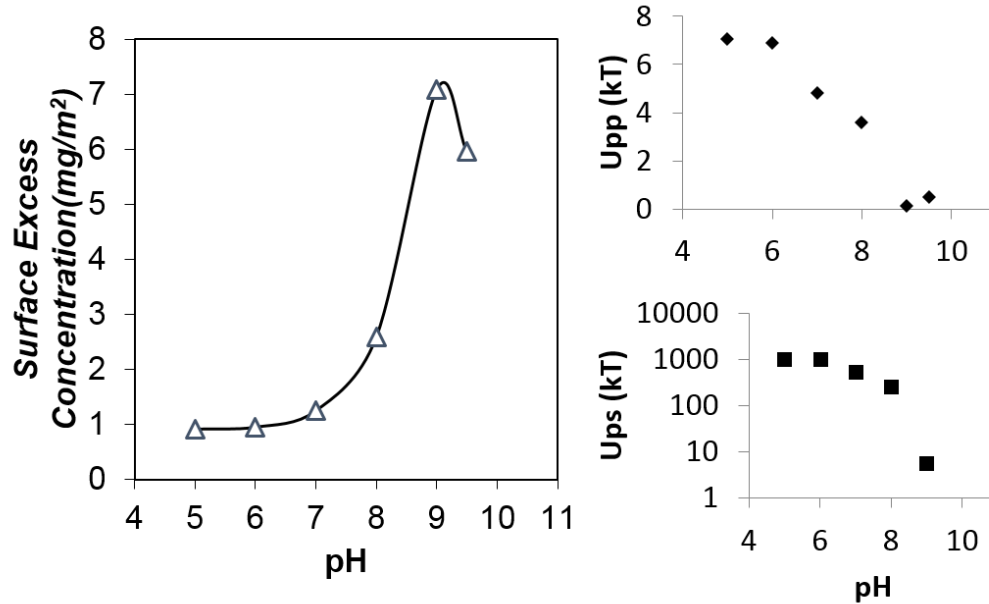


Figure 4.7. Electrostatic RSA calculations for SiO₂-g-PDMAEMA adsorption to oppositely charged silica surfaces in 1 mM NaCl. *Left:* Surface excess concentration, exhibiting the same qualitative behavior captured experimentally via direct adsorption ellipsometry and QCM-D. *Top right:* Estimated particle-particle electrostatic interaction energy. *Bottom right:* Estimated particle-surface electrostatic interaction energy.

The suitability of using the measured hydrodynamic radius of SiO₂-g-PDMAEMA in suspension to represent its size after adsorption merits further

consideration. Agreement of measured surface excess concentrations with electrostatic RSA predictions support the idea that the SiO₂-*g*-PDMAEMA particles behave essentially as charged spheres, with little deformation, when adsorbing to silica. This is further supported by molecular dynamics simulations of multi-arm polyelectrolyte star polymers adsorbed at oppositely charged interfaces by Konieczny and Likos.¹⁹ The conformation of the polyelectrolyte stars in the simulation was controlled by the number of arms f and the dimensionless surface attraction parameter $\sigma_0 l^2/e$, where σ_0 is the surface charge density. For the large number of chains on the SiO₂-*g*-PDMAEMA BGNPs ($f > 500$) and the relatively low dimensionless surface charge ($\sigma_0 l^2/e < 0.005$) in the current experiments, those simulations would indicate that the particles should be very weakly deformed at the surface, essentially retaining their dimensions after adsorption.

4.2.4 *Streaming potential*

Streaming potential measurements were conducted with silica surfaces before and after adsorption of linear PDMAEMA or SiO₂-*g*-PDMAEMA (grafting density 0.46) in 1 mM NaCl solutions. **Figure 4.8** shows that the zeta potential of bare silica became increasingly negative with increasing pH due to silanol de-protonation, leveling off at approximately -120 mV above pH 7. Zeta potentials corresponded to negative surface charge densities of approximately 30 nm² per charge at pH 5 and 10 nm²/charge at pH 9, calculated using Guoy-Chapman theory. These values are in agreement with prior studies of the silica/water interface.^{20,21}

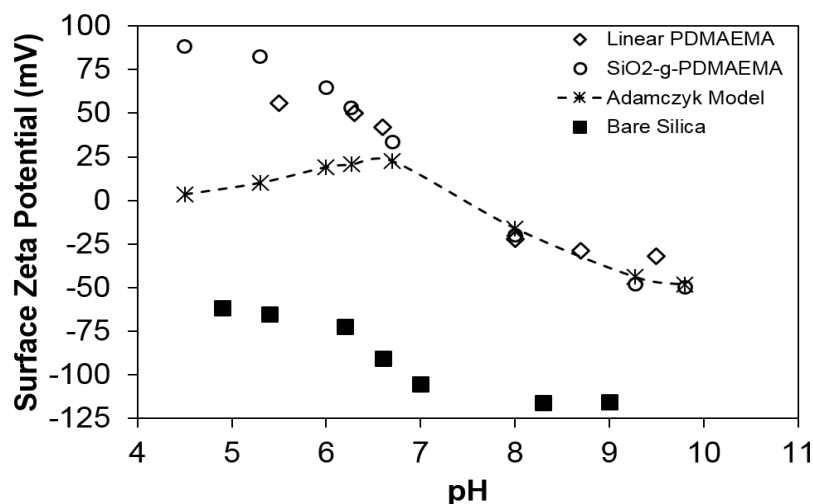


Figure 4.8. Zeta potential of silica surfaces in 1 mM NaCl measured by the rotating disk streaming potential method. Polymer concentrations are 2 ppm. Predictions from Adamczyk model²² for streaming potential of particle-coated surfaces are plotted using measured surface coverages from ellipsometry, particle size from DLS, and particle zeta potential for SiO₂-g-PDMAEMA.

Streaming potential measurements of silica surfaces in contact with a 1 mM NaCl, 2 ppm linear PDMAEMA solution confirm polymer adsorption to silica as indicated by the positive apparent zeta potential measured at lower pH. Adsorption at the very low concentration is consistent with the high-affinity nature of electrostatically driven polyelectrolyte adsorption. Adsorption at pH 5.5, below the PDMAEMA pK_a , reversed the net charge of the interface, yielding an apparent zeta potential after adsorption of +60 mV. At pH > pK_a , the net surface charge was not reversed, but the -35 mV apparent zeta potential at pH 9.5 was significantly less negative than the bare silica zeta potential, indicating that PDMAEMA did adsorb to some extent despite its low charge density at pH 9.5.

Streaming potential measurements after adsorption of 2 ppm SiO₂-g-PDMAEMA on silica from 1 mM NaCl indicate similar qualitative behavior as

linear PDMAEMA: charge over-compensation at low pH and under-compensation at high pH. A -55 mV zeta potential was obtained at pH 9, which is again significantly less negative than the bare silica surface.

We attempt to interpret the streaming potential measurements in the context of the Adamczyk model²³ for electrokinetics of particle or macromolecule coated surfaces. Here, the coated surface streaming potential in shear flow is approximated as a linear function of the particle (subscript p) and bare surface (subscript s) zeta potentials:

$$\zeta_{p+s} = F_s(\theta)\zeta_s + F_p(\theta)\zeta_p \quad (4.5)$$

Here, the coefficients F_s and F_p are functions of the coverage:

$$F_s = e^{-C_1\theta} \quad F_p = \frac{1}{\sqrt{2}}(1 - e^{-\sqrt{2}C_2\theta}) \quad (4.6)$$

and the constants C_1 and C_2 depend on the particle size and ionic strength. For particles where the size is much larger than the Debye length (here, $\kappa a > 5$), C_1 and C_2 assume values of 10.2 and 6.5, respectively. Using the experimentally measured bare surface and particle zeta potentials, along with the coverage as measured by ellipsometry, we can predict the coated-surface zeta potential. These predictions are also shown in **Figure 4.8**. The Adamczyk model shows good agreement with the data at intermediate pH, but strongly under predicts the streaming potential at low pH. The surface coverage is low ($\sim 5\%$) at pH 5, and the model would predict a streaming potential intermediate to the particle and surface values. The measured streaming potential is very high, which requires a high surface coverage in the context of the model. These differences possibly arise from the soft brush layer on the particles resulting in differences between the

measured zeta potential and the actual potential at the particle edge. Simulations using the exact soft-particle electrokinetic theory of Hill suggest that SiO₂-*g*-PDMAEMA can assume a potential of up to + 115 mV, or 40% higher than measured, at the brush edge. This would somewhat reconcile the streaming potential measurements and the theory predictions. Note: no fitting is performed.

4.3 Thermally driven adsorption

Section 4.2 above provides an overview of how electrostatics govern the direct adsorption of SiO₂-*g*-PDMAEMA to an oppositely charged silica surface at room temperature, owing to PDMAEMA's pH and ionic strength dependent degree of ionization. PDMAEMA also exhibits a *lower critical solution temperature*, and the thermo-responsiveness of SiO₂-*g*-PDMAEMA suspensions was presented in Section 4.1.2 and **Figure 4.3**. The ability to additionally modify the SiO₂-*g*-PDMAEMA/solvent interaction via temperature should enable further enhancement of adsorption, which is desirable in forming densely packed SiO₂-*g*-PDMAEMA layers that are only achievable at room temperature in a sharp pH window. This effect has been observed previously for adsorption near the CFT for pluronic solutions on silica²⁴. The following section studies the influence of adsorption temperature on the deposition of SiO₂-*g*-PDMAEMA.

4.3.1 AFM and ellipsometry

The effect of temperature on the adsorption of SiO₂-*g*-PDMAEMA to silica is first assessed by AFM imaging and *ex-situ* ellipsometry. Here, SiO₂-*g*-PDMAEMA is adsorbed at different pH and temperature in order to identify whether or not adsorption can be further enhanced by temperature. **Figure 4.9**

shows representative AFM images of adsorbed layers formed at room temperature and temperatures approaching the CFT in 10 mM NaCl. Visualizing the layers using AFM allows for a direct assessment of the density of adsorbed particles on the surface. At pH 8.5 and 25 °C, the sample is being adsorbed at a temperature that is 20 – 30 °C below the CFT, or $CFT - T = 20$ to 30 °C. The particles are still charged to an extent and adsorb in a relatively patchy arrangement on the surface. At pH 9.1 and 25 °C, the sample is again being adsorbed well below the CFT, but here we are adsorbing near the isoelectric point and pH-adsorption maximum. Enhanced particle deposition is evidenced in the AFM image. Finally, adsorption is conducted at pH 9.1 and 37 °C, at the pH maximum and also a temperature that is just below the CFT, or $CFT - T = 3$ to 15 °C. The AFM image of this adsorbed layer indicates further adsorption has occurred, and the surface is densely packed with nanoparticles. Some multi-particle aggregates occur on the surface, but adsorption appears to occur homogeneously across the surface in a randomly distributed monolayer.

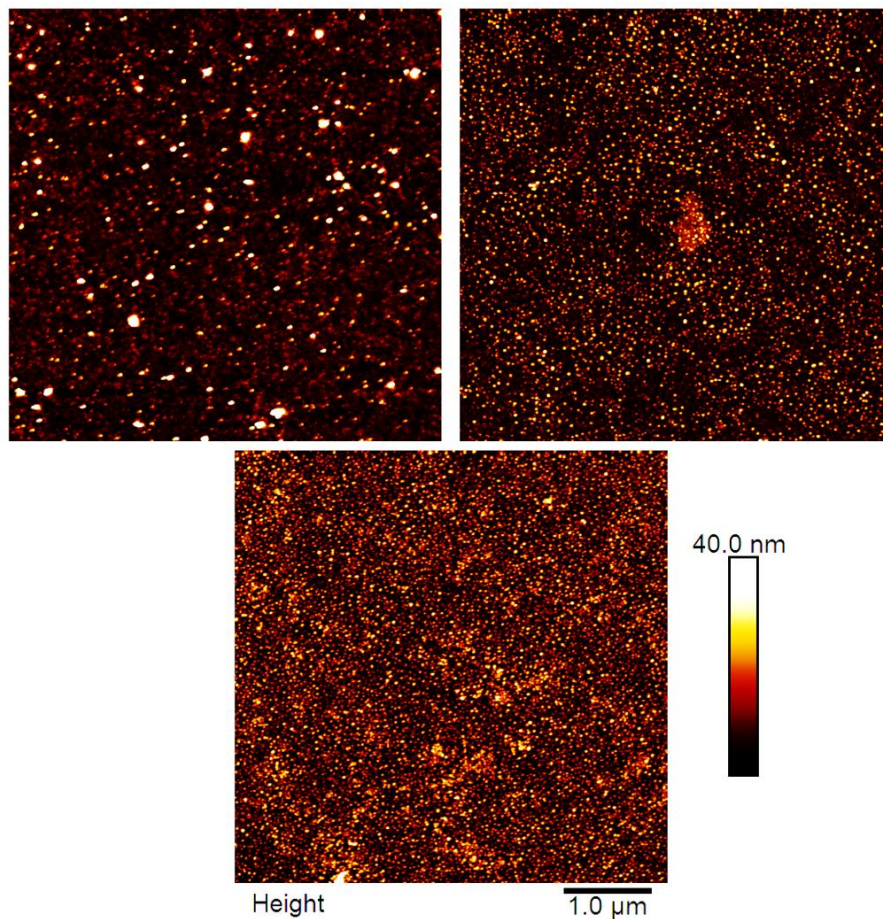


Figure 4.9. AFM height images in air (5μm x 5μm) of SiO₂-g-PDMAEMA adsorbed on silica. *Top left:* 10 mM, pH 8.0, 25 °C. *Top right:* 10 mM, pH 9.1, 25 °C. *Bottom:* 10 mM, pH 9.1, 37 °C. Adsorption time was 1 hour.

Ellipsometry thicknesses and particle counting in AFM are summarized in **Table 4.1** Dry characterization of SiO₂-g-PDMAEMA adsorbed layers. Both methods show the same relative changes in adsorbed amounts. At room temperature, the measured adsorbed amount is ~6 times higher by adsorbing at pH 9 than it is at pH 5, owing again to electrostatics. But increasing the temperature by 10-15 °C at pH 9 leads to a further doubling of the adsorbed amount. Particle separations estimated from the number density measured by AFM indicate that under the dense particle packing, the average center-to-center

separation distance is approximately 65 nm. Accounting for the collapsed particle size of 30 nm, the average edge-to-edge separation distance is 35 nm, or very close to the particle diameter with a collapsed brush.

Table 4.1 Dry characterization of SiO₂-*g*-PDMAEMA adsorbed layers

Solution pH	Adsorption Temperature (°C)	CFT (°C)	Dry Ellipsometry Thickness (nm)	# adsorbed particles - AFM (μm²)	avg. center-to-center distance (nm)
5	25	> 100	0.63 +/- 0.2	22 +/- 5	213
9	25	40-55	3.4 +/- 0.4	120 +/- 16	91
9	37	40-55	7.3 +/- 0.8	240 +/- 30	65

4.4 Observations on SiO₂-*g*-PDMAEMA adsorption hysteresis

4.4.1 pH processing and sequential adsorption

Figure 4.5 represented experiments where SiO₂-*g*-PDMAEMA particles were adsorbed directly to a bare surface at a specified pH. The adsorption was sharply peaked near pH 9. Given the surface modification applications that motivate this research, it would be desirable to achieve even larger surface coverages and to do so over a broader pH range. Thus we examined sequential adsorption processes where particles were adsorbed at one pH, followed by post-adsorption pH variations with particles still in suspension. **Figure 4.10** shows the results of experiments where SiO₂-*g*-PDMAEMA particles were first adsorbed at 100 ppm concentration at a pH of ~5 to 6 followed by incremental increases up to pH 10, and vice-versa, where adsorption was initiated at the pH-adsorption maximum near pH 9.1 to 9.2 followed by incremental decreases down to pH 4 to

6. Interestingly, these sequential adsorption experiments exhibited different pH responses than the direct adsorption experiments.

For the increasing pH method, the surface excess concentration increased linearly with pH for all salt concentrations but more strongly than it did in the direct adsorption experiments. At pH 8 the surface excess concentration was approximately 2.5 mg/m^2 for 10 mM NaCl adsorption, whereas direct adsorption at pH 8 yielded surface excess concentrations that ranged from 0.8 at 1 mM ionic strength to 1.8 mg/m^2 for 100 mM ionic strength. The maximum in surface excess concentration displayed by the sequential adsorption process was significantly less sharp than the maximum in direct adsorption. At pH 10, the surface excess concentration remained notably higher for sequentially adsorbed particles than it did for directly adsorbed particles for all salt concentrations. **Figure 4.10** shows that the calculated surface coverage varied between 0.05 and 0.27 and with a maximum at $\sim \text{pH } 7 - 8$.

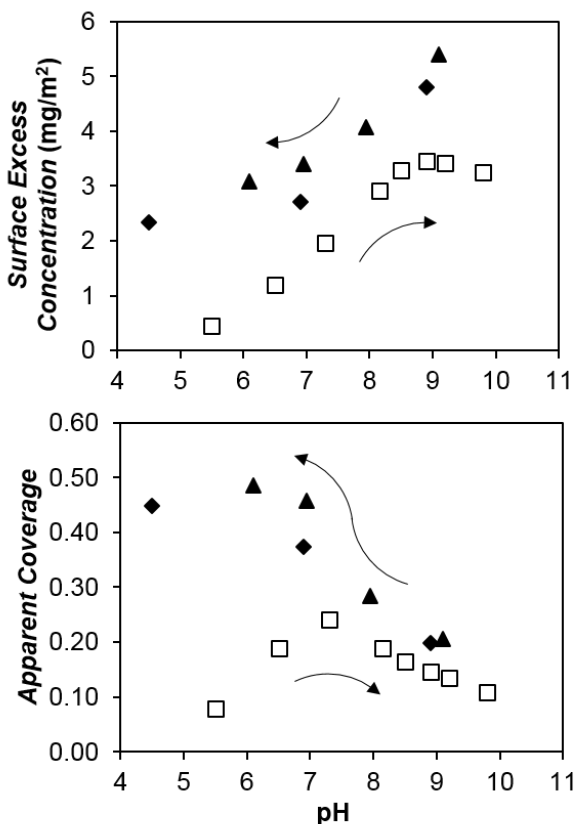


Figure 4.10. Sequential adsorption measurements performed either by step-wise pH increases starting at a pH 5 (unfilled) or step-wise pH decreases starting at pH 9.0 – 9.2 (filled) measured in situ by ellipsometry. *Top:* Adsorbed mass. *Bottom:* Apparent coverage, calculated from the surface excess concentration and the bulk suspension hydrodynamic size and particle molecular weight: $\theta = \Gamma \pi R_h^2 M_w / N_A$.

Both the surface excess concentration and the surface coverage were higher for all pH values when the initial adsorption was conducted at the pH maximum and then decreased. By first adsorbing near pH 9, the maximum number of particles would be allowed to adsorb. Increasing protonation would not only build up charge in the brush but also cause the grafted brushes to swell with decreasing pH. The strengthened lateral repulsions at lower pH caused some particles to desorb, but still more particles remained adsorbed than were able to adsorb directly to the bare silica at any given pH, by circumventing the

electrostatic RSA limitations. The result of this increased adsorption via the sequential pathway would produce a significant increase in surface coverage when the brush swelling is taken into account, as shown in **Figure 4.10**.

Sequential adsorption produced an apparent surface coverage as large as $\theta = 0.49$, approaching the RSA jamming limit for neutral rigid spheres of $\theta_{hd} = 0.55$. This occurred as each pre-adsorbed BGNP swelled to exclude more area on the surface.

It is apparent when comparing **Figure 4.5** and **Figure 4.10** that SiO₂-*g*-PDMAEMA adsorption is hysteretic in the sense that it depends on the pH history of the adsorption system. This contrasts with linear PDMAEMA, which exhibited reversible pH response (**Figure 4.4**). We attribute this behavior to hindered dynamics caused by strong multi-segment binding between polymers in the brush and the surface. Linear polymers are conformationally flexible relative to chains within the brush of SiO₂-*g*-PDMAEMA, and thus can re-arrange and desorb from the surface more easily, leading to reversible pH effects. The hysteretic adsorption behavior indicates that either the brush nanoparticles have significantly slower relaxation times than linear polymers, or that the presence of a dense brush near the surface hinders the local pH from equilibrating with that of the bulk. Both mechanisms could support non-equilibrium adsorbed layers.

4.4.2 Thermal hysteresis

Thermally driven adsorption of SiO₂-*g*-PDMAEMA on silica is further investigated using *in-situ* QCM-D with a programmed temperature cycle. These experiments assess the extent of adsorption upon step-wise changes in solution

temperature. Measurements are made upon heating and cooling to probe any thermally-induced hysteretic effects. A typical experiment is shown in **Figure 4.11** utilizing a temperature program that goes from 25 – 45 °C at increments of 5 °C and holds the system at each temperature set-point for 30 – 60 minutes. The temperature program is executed first with only pure solvent to capture the baseline frequency and dissipation shifts associated with changes in the fluid density and viscosity. After heating and cooling back to room temperature, SiO₂-*g*-PDMAEMA is introduced and allowed to adsorb for ~ 1 hour. SiO₂-*g*-PDMAEMA is not rinsed from suspension, and the temperature program is initiated again. Frequency and dissipation shifts for adsorption during temperature steps can be obtained by subtracting the pure fluid response. Adsorption is initially conducted with 100 ppm SiO₂-*g*-PDMAEMA suspensions in 10 mM NaCl at four different pH conditions: pH 5.0, 8.0, 9.0, and 9.2. This produces adsorbed layers with varying initial coverages, as can be seen by the differences in frequency shift for the first filled symbol of each series in **Figure 4.12**. The data here is plotted against the temperature relative to the CFT, and each series is at a different pH throughout. At the lowest pH, farthest from the CFT, there is very little change in adsorption as temperature is ramped from 25 to 45 °C, due to very little change in the particle stability in water. At pH 9 and 9.2, the temperature is ramped closer to the CFT of the suspension and therefore these layers exhibit the largest changes upon temperature ramping. At pH 9, adsorption is increased and upon cooling there is strong hysteresis. This hysteresis is also observed for pH 9.2, and the inset shows the magnitude of irreversibly added

particles increases with pH as the suspension becomes the most thermally responsive. The excess frequency shifts from hysteresis correspond to an extra $\sim 1.5, 3.0$, and 2.7 mg/m^2 of adsorbed mass for pH 8, 9, and 9.2 respectively. Thus, temperature processing via slow temperature quenching provides another route for enhancing deposition.

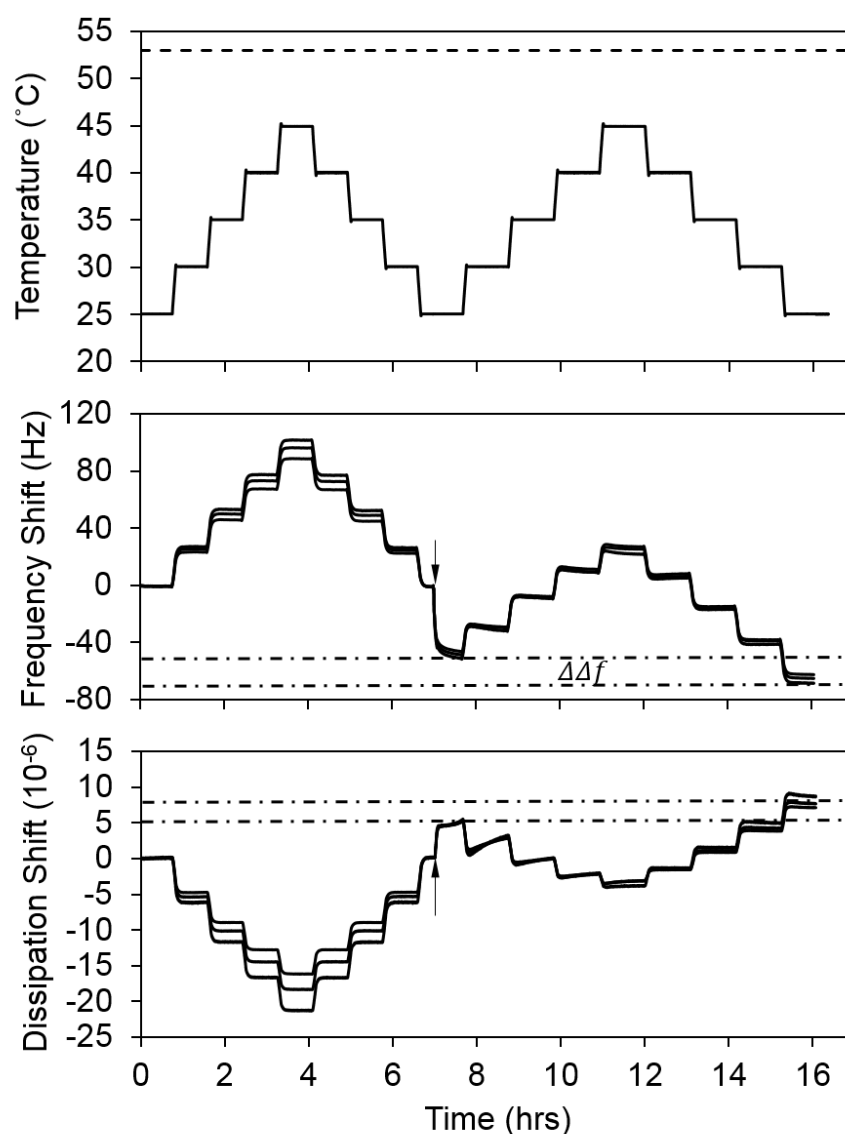


Figure 4.11. Temperature cycled adsorption of SiO_2 -*g*-PDMAEMA to silica in 10 mM NaCl at pH 9.0 measured by QCM-D. *Top:* Temperature profile, heating rate of $1^{\circ}\text{C}/\text{min}$ between 5°C increments. Dashed line represents the SiO_2 -*g*-PDMAEMA CFT, 53°C , for this sample measured immediately prior to QCM-D.

Middle: Frequency shift for pure solvent ($t = 0 - 7$ hr), during adsorption (arrows, $t = 7 - 7.5$ hr), and heating/cooling in the presence of adsorbed and suspended SiO_2 -*g*-PDMAEMA ($t = 7.75 - 16.5$ hrs). *Bottom:* Dissipation shifts. The fifth, seventh, and ninth overtones are displayed. Note: the dashed-dot lines in the middle and bottom panels represents the difference between initial adsorbed amount at 25 °C and the adsorbed amount after temperature cycling and return to 25 °C. This can be considered the excess adsorbed amount due to adsorption hysteresis during thermal processing.

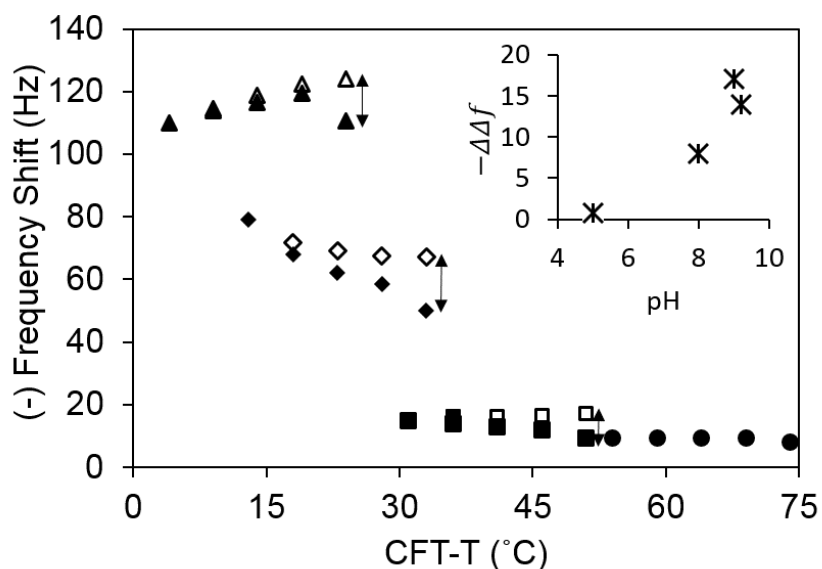


Figure 4.12. Adsorption of SiO_2 -*g*-PDMAEMA as a function of temperature and pH measured by QCM-D. SiO_2 -*g*-PDMAEMA suspension are 0.1 mg/mL in 10 mM NaCl with: pH 5.75 (circles, CFT = 99), pH 8.0 (squares, CFT = 76), pH 9.0 (diamonds, CFT = 58), pH 9.2 (triangles, CFT = 51). Temperature cycle on heating (filled symbols) and cooling (unfilled) from 25 – 45 °C. Data is shown for the fifth overtone number. *Inset:* Excess frequency shift due to thermal hysteresis, indicated by the arrows.

4.4.3 Drying and re-solvation of layers

Another important factor in considering hysteretic behavior of adsorbed SiO_2 -*g*-PDMAEMA is the ability to dry and re-solvate layers. It is well known that contact lines and strong capillary forces can strongly effect deposition of nanoparticles and colloids. Therefore, it is important to test whether or not the particles are pulled off the surface or rearrange in response to drying of the layer

and placing them back under an aqueous solution. **Figure 4.13** shows AFM images obtained of temperature-processed adsorbed layers in air after initial deposition and drying, then bathed in solution upon re-solvation. Imaging is done in PF-QNM mode, and the topographical height image as well as the deformation image are shown. The deformation image is sensitive to the swelling state of the brush and can resolve more clearly the edge of the brush. The height profile mainly captures the rigid portion of the particle. The representative AFM images show very little, if any, change in the number density of adsorbed particles upon drying and re-solvating. Additionally, swelling the particles does not appear to induce desorption of particles due to strengthened brush-brush steric and electrosteric repulsions. A number of surface dimer aggregates remain joined before and after solvation, indicating that some strong interpenetration occurs either during temperature-driven deposition or in the drying process. Nevertheless, the adsorbed particles do re-swell with solvent as shown in **Figure 4.14**. The profiles shown here are azimuthally-averaged deformation profiles mainly resolving the portions of the brush that extend parallel to the surface. It has been shown previously in our group that the chains in polymer-grafted nanoparticles are more easily deformable to bending than compression²⁵, thus deformation imaging emphasizes the bending component of the spherical brush. It is clear from the brush deformation profiles that the swollen brush is not only more extended, but it is also mechanically softer as evidenced by the larger deformation values. The confirmation of particle re-swelling suggests that particle-surface attraction is strong enough to retain adsorbed particles despite the

strong repulsions between particles that reside closely on the surface. This is in agreement with the estimations of the particle-particle repulsion energy and particle-surface attraction energy in the E-RSA model given in **Figure 4.7**, where repulsions and attractions are $5\text{ }kT$ and $800\text{ }kT$ at pH 7, respectively.

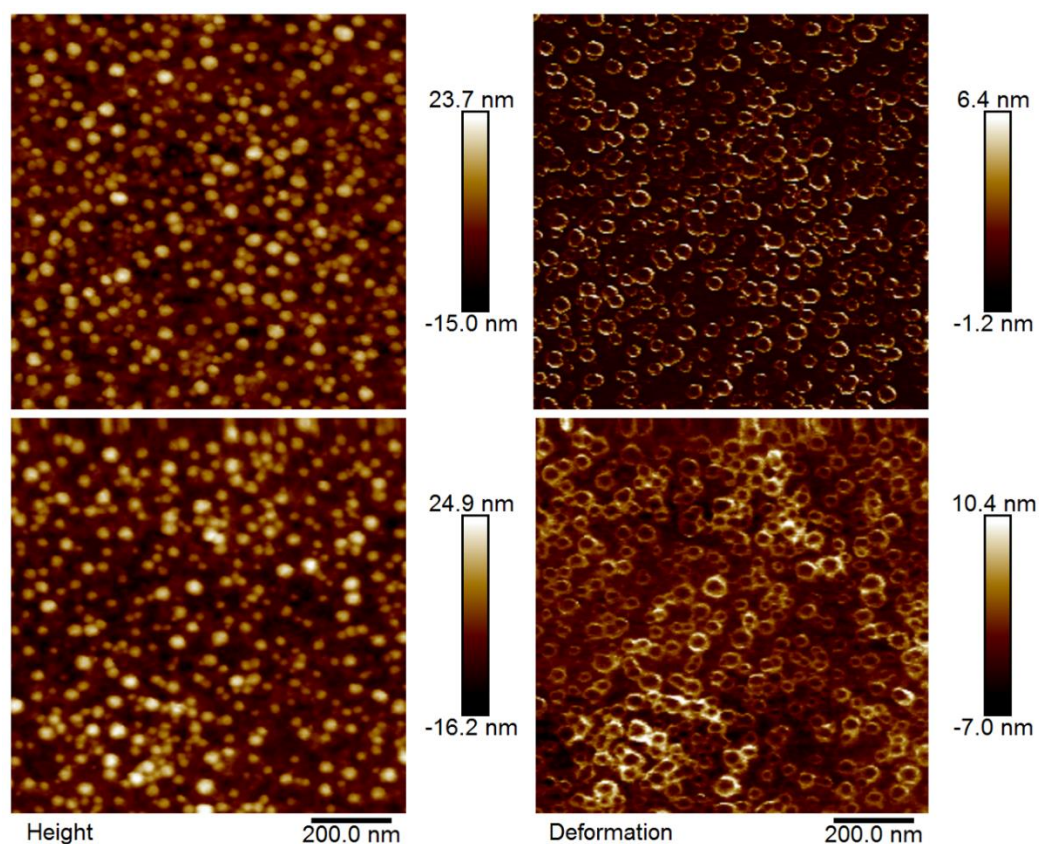


Figure 4.13. PF-QNM images of SiO_2 -*g*-PDMAEMA adsorbed layers imaged in air (*top row*) and in 10 mM NaCl, pH 7 (*bottom row*). Both the height (*left*) and deformation (*right*) images are shown. Image analysis across multiple spots on the surface indicates that no particle desorption occurs during drying and re-solvation of the densely packed layers.

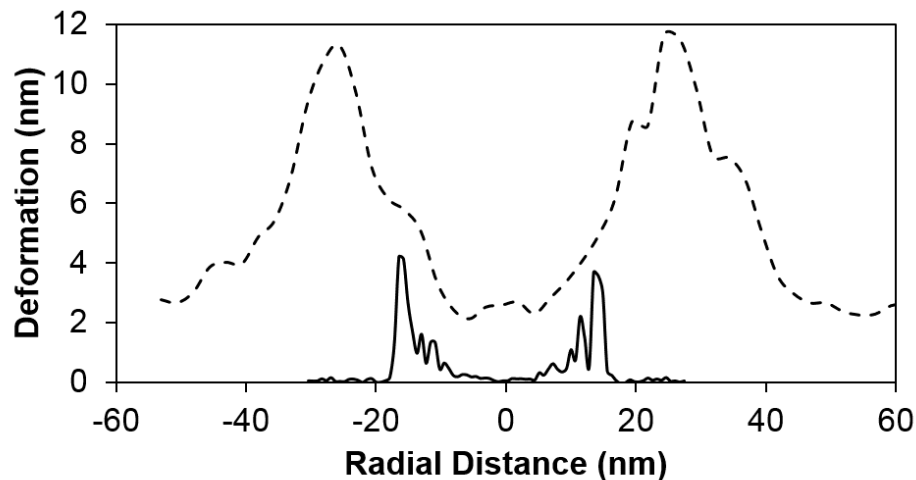


Figure 4.14. Azimuthally-averaged PF-QNM deformation profiles of SiO₂-*g*-PDMAEMA nanoparticles adsorbed on a silica surface. The average profile is shown for $n = 5$ particles on the surface. Solid line is the profile of particles imaged in air, and the dashed line is the profile of particles swollen with 10 mM NaCl at pH 7.0. The deformation profiles are not offset, and the vertical shift in the baseline deformation to ~ 2.5 nm upon measuring in liquid is due to the double-layer repulsion between the sharp AFM tip and silica surface. Distance zero is the center of the particle.

4.5 Conclusions

PDMAEMA brush-grafted silica nanoparticles demonstrate size and charge that are responsive to temperature, pH and ionic strength. The particles readily adsorb to silica surfaces as indicated by ellipsometry, steaming potential, QCM-D, and AFM measurements. The PDMAEMA brush-grafted nanoparticles display a sharp pH induced adsorption maximum in 1 and 10 mM NaCl, but a broader maximum in 100 mM NaCl. The trends in the experimental results for direct adsorption of these soft charged particles to an initially bare silica surface are consistent with the expectations for electrostatic random sequential adsorption, where long range repulsions inhibit adsorption relative to uncharged particles.

Significant qualitative differences in electrostatic adsorption behavior exist between the brush grafted nanoparticles and the chemically similar linear polyelectrolyte. Whereas linear PDMAEMA adsorption is nearly completely prevented under the weak adsorption strength conditions of high pH and elevated ionic strength, a significant amount of PDMAEMA-grafted nanoparticles can adsorb under those conditions due to multi-chain attachment and a less unfavorable entropy of adsorption compared to the linear polyelectrolyte.

PDMAEMA brush-grafted nanoparticle adsorption is strongly hysteretic, while linear PDMAEMA adsorption is fully reversible, with respect to the pH history of the layer. Adsorption at high pH, where lateral repulsions are minimized and the brush grafted nanoparticles assume their most compact form, produces a maximum surface excess concentration. Adsorption can be further enhanced by elevating temperature while remaining below the CFT of the brush-grafted nanoparticle suspension. The adsorption is sufficiently tenacious that most of the particles remain adsorbed during drying and subsequent solvation or during decreases in pH to charge and swell the brush and produce a large area fraction surface coverage. The production of adsorbed brush-grafted nanoparticle layers that display a wide range of surface coverage, charge and swelling is expected to be useful in the development of responsive surface coatings.

4.6 References

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5. Surface forces between adsorbed layers of polymer brush nanoparticles

This chapter presents the measured interaction forces that arise when surfaces are covered with polymer brush nanoparticles and brought into contact. This primarily involves colloidal probe normal and friction force measurements under different adsorbed layer conformations and solution conditions. The force measurements are interpreted using our understanding of the polymer brush nanoparticle properties in the bulk and their adsorbed layer properties at a surface. These aspects are discussed in **Chapter 3** for non-ionic star polymers and **Chapter 4** for polyelectrolyte grafted nanoparticles. This Chapter will discuss the interaction forces that arise between *single-component* brush nanoparticle adsorbed layers, and how processing of these layers into non-equilibrium conformations can be used to manipulate both adhesion and friction. Control of adhesion and friction by polymer brush nanoparticles is enabled by their sub-monolayer surface coverages and the resulting tunable bridging interactions. Attention is given to the effects of surface coverage on the interaction forces, and criteria are established for roughly predicting the stimuli-responsive adhesion and friction properties for these systems.

5.1 Non-ionic Star PEO

Star PEO adsorption has been described in detail in **Chapter 3** and additionally in **Chapter 7**. Adsorption data shows that Star PEO adsorbs readily to silica in the range pH 4.5 to 8.7. At higher pH, silica adsorption is prevented by a sub-critical density of surface silanol sites. Ellipsometry and AFM suggest that

Star PEO surface coverage can reach $\sim 60 - 70\%$, forming a densely packed brush-like layer. Normal force profiles for Star PEO on silica are shown in **Figure 5.1**. Measurements are made during the adsorption of Star PEO and features of the adsorption kinetics can be identified in the force profiles.

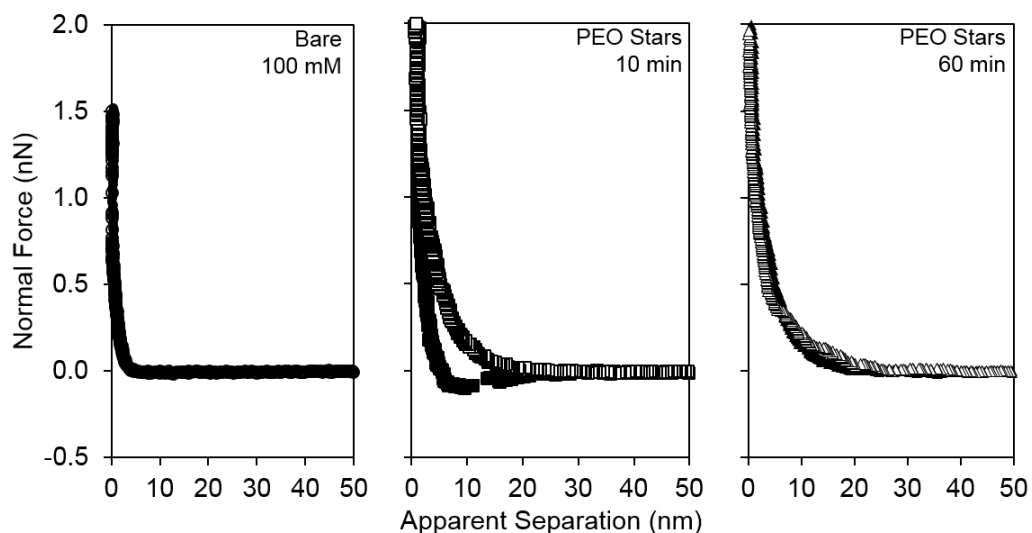


Figure 5.1. Normal force profiles between a $10\ \mu\text{m}$ glass colloidal probe and a flat silica surface across $100\ \text{mM}$ NaCl and during PEO star adsorption from a $0.1\ \text{mg/mL}$ suspension. *Left:* double layer repulsion between bare probe and bare surface ($\kappa^{-1} = 0.96\ \text{nm}$). *Middle:* forces after 10 minutes of PEO star adsorption, showing bridging across low-coverage adsorbed layers. *Right:* forces after 60 minutes of PEO star adsorption, with pure steric repulsions resulting from a dense adsorbed layer.

Initial measurements of the bare surfaces in $100\ \text{mM}$ NaCl show pure double layer repulsions, with a measured decay length $\kappa^{-1} = 0.96\ \text{nm}$, in excellent agreement with the expected Debye length for $100\ \text{mM}$ NaCl of $\kappa^{-1} = 0.97\ \text{nm}$. Star PEO is introduced at a concentration of $0.1\ \text{mg/mL}$, on to the adsorption plateau for achieving surface saturation. After 2 minutes of adsorption, slight adhesion is measured between the surfaces indicating the presence of a sub-

monolayer Star PEO adsorbed layer. The onset of repulsions occurs at 25 nm, indicating steric and no longer purely electrostatic interactions. The adsorbed layer is fully developed after 60 minutes, where purely repulsive forces are observed and adhesion is no longer present. This confirms the presence of a densely packed adsorbed layer.

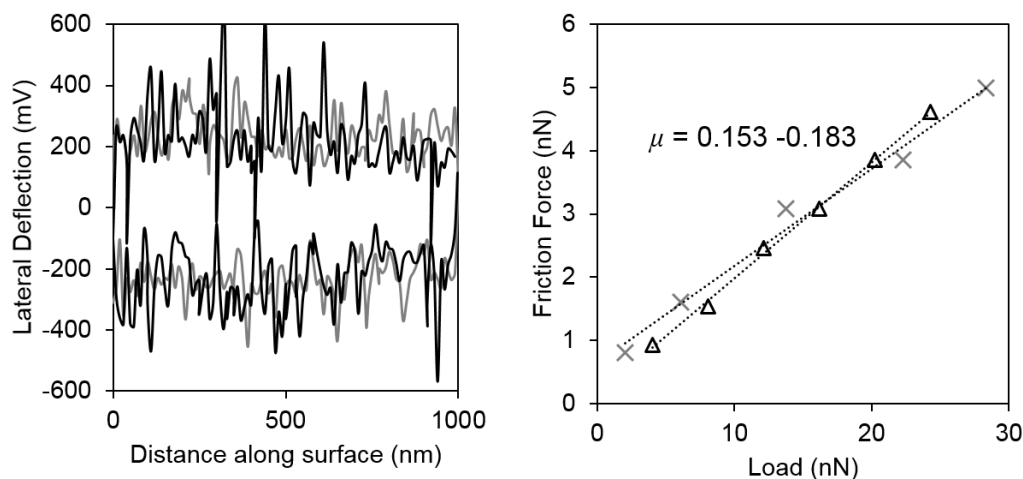


Figure 5.2. Friction properties between a 10 μm glass colloidal probe and flat silica surface bearing adsorbed Star PEO layers. *Left:* Raw lateral force traces at an applied load of 13.7 nN and a sliding speed of 1 $\mu\text{m/s}$. Forces are obtained in 1 mM NaCl (grey) and 100 mM NaCl (black). *Right:* Friction versus load for PEO stars in 1 and 100 mM NaCl.

Friction forces between Star PEO adsorbed layers are also measured and shown in **Figure 5.2**. Friction measurements are performed in 1 and 100 mM NaCl to investigate the role of salt concentration on friction. Friction loops obtained at an applied load of 13.7 nN and a sliding speed of 1 $\mu\text{m/s}$ indicate very little difference between the friction forces exerted in 1 and 100 mM NaCl. Upon compression of the layers at multiple applied loads, the coefficients of friction are measured to be 0.153 and 0.183 in 1 and 100 mM NaCl. The slight differences in

friction coefficient can be attributed to slightly worse solvent quality at the higher salt concentration. These coefficients of friction are comparable to other similar adsorbed, brush-like PEO materials studied in the literature. Bottle-brush polymers with cationic poly(lysine) backbones and PEO side chains¹ have been reported to have coefficients of friction between 0.1 and 0.4, and similar bottle-brushes with METAC cationic backbones and PEO side chains² have reported between 0.01 and 1. The normal force profiles show no damage after friction, also indicating that the layers are tenaciously adsorbed. Thus, star PEO is feasible as an aqueous lubricant. Further friction forces for star PEO are discussed later in the context of mixed brush nanoparticle adsorbed layers.

5.2 Cationic, PDMAEMA-grafted silica nanoparticles

SiO₂-*g*-PDMAEMA exhibited robust temperature and pH-responsiveness with respect to its bulk suspension properties and ability to adsorb at an oppositely charged interface, as discussed in **Chapter 4**. The implications of adsorbed layer properties and the resulting surface forces is discussed in the following section.

5.2.1 Friction control by pH-processing

One of the major findings in **Chapter 4** was the observation that SiO₂-*g*-PDMAEMA adsorption largely results in sparsely populated surface layers on silica, owing to the delicate balance of lateral particle-particle repulsions and particle surface attractions that vary with solution pH. The result is a narrow pH window for maximum particle packing of SiO₂-*g*-PDMAEMA onto the surface. Outside of this window, low coverage SiO₂-*g*-PDMAEMA layers are formed. High coverage layers can be formed utilizing strong adsorption hysteresis effects

owing to kinetically-hindered desorption of the particles upon rinsing to different pH values. The above features are shown via force curve measurements displayed in **Figure 5.3**.

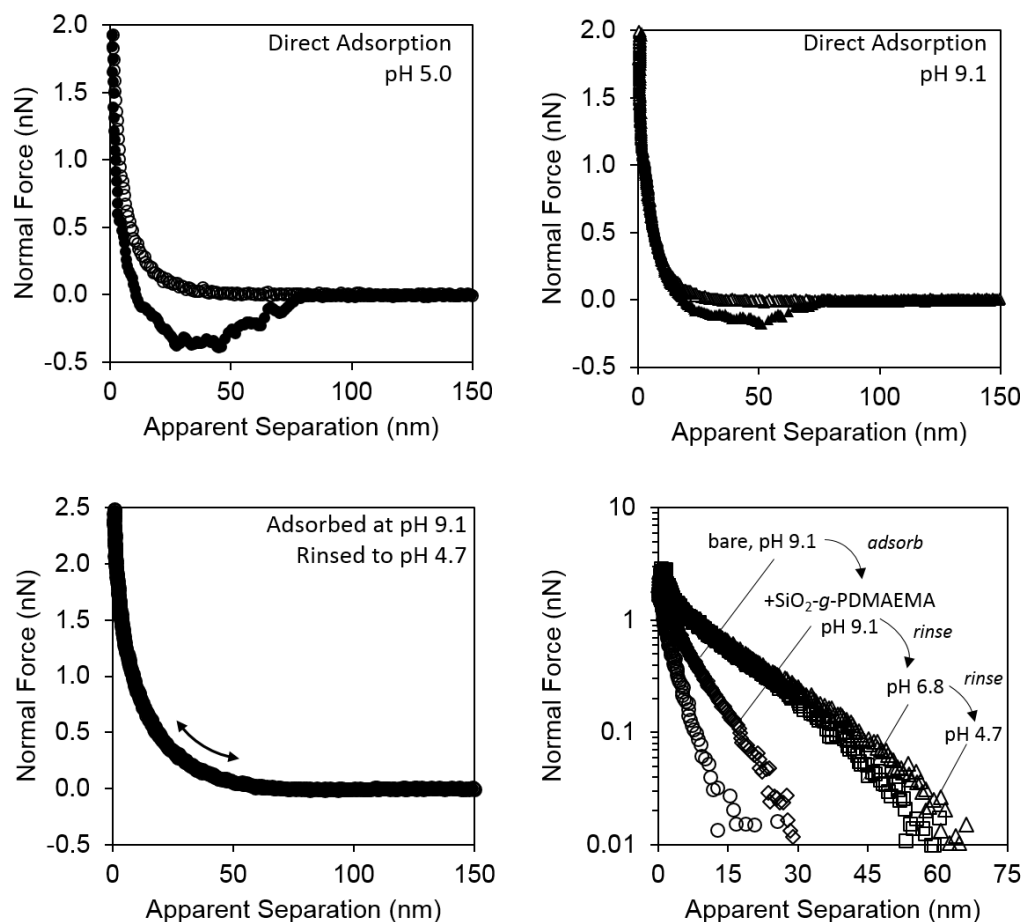


Figure 5.3. Normal force versus distance profiles between a 20 μm silica colloidal probe and flat silica surface, each bearing adsorbed $\text{SiO}_2\text{-g-PDMAEMA}$. Unfilled symbols on approach and filled symbols on retraction. *Top left:* $\text{SiO}_2\text{-g-PDMAEMA}$ adsorbed directly at pH 5.0, resulting in low coverage layers of positively charged particles. *Top right:* direct adsorption at pH 9.1, corresponding to a higher coverage but relatively uncharged particles. *Bottom right:* Approach curves during a pH-processing experiment, showing pure double-layer forces for the bare surfaces followed by adsorption at pH 9.1 and rinses to pH 6.8 and pH 4.7. *Bottom left:* Purely repulsive approach and retract curves after rinse cycle to pH 4.7.

Direct adsorption of SiO₂-*g*-PDMAEMA to the silica surfaces at pH 5.0 and measurement of the normal forces reveals attractive bridging after the surfaces are brought into contact and pulled apart. This bridging attraction is a consequence of a low surface coverage on both the probe and the surface. Recall, the slow coverage at pH 5.0 is due to strong lateral electrostatic repulsions between adsorbed particles. The adhesion curve at pH 5.0 exhibits multiple pull-off events that likely correspond to the breaking of SiO₂-*g*-PDMAEMA arms that have bridged across the opposing surface. Direct adsorption of SiO₂-*g*-PDMAEMA at pH 9.1 is also shown in **Figure 5.3**. A 6 – 8 fold increase in adsorbed amount is expected at pH 9.1 compared to the low adsorbed amount reached at pH 5.0. Despite the increase in adsorption at pH 9.1, attractive forces still arise in the normal force profiles. This is still likely caused by insufficient surface coverage and bridging of SiO₂-*g*-PDMAEMA across the surfaces. The maximum adhesion force is approximately 3 times less at pH 9.1 than at pH 5.0, indicative of the weakened bridging attraction per adsorbed SiO₂-*g*-PDMAEMA. Less polymer segment extension and contact with opposing surface in a particle bridge occurs when the SiO₂-*g*-PDMAEMA brush is collapsed.

pH processing was shown to be a viable method for overcoming the limitations of low coverages in directly adsorbed SiO₂-*g*-PDMAEMA layers. This method involves trapping the particles in a non-equilibrium conformation by adsorbing at the pH-maximum and rinsing to charge and swell adsorbed SiO₂-*g*-PDMAEMA. This method can achieve surface coverages of approximately 50%³ – substantially higher than direct adsorption. **Figure 5.3** also shows the difference

between *direct adsorption* and *pH-processing*. Approach curves on a *log-lin* plot are shown for bare silica in 10 mM NaCl, displaying characteristic double layer forces with a decay length of 2.9 nm, close to the expected Debye length of $\kappa^{-1} = 3.1$ nm. Adsorption of SiO₂-*g*-PDMAEMA at pH 9.1 results in longer range forces than the bare surfaces, and subsequent rinses to pH 6.8 and pH 4.7 show further swelling and shifting of the repulsions to longer range and non-double layer electrosteric repulsions. The force curves for the pH-processed layer at pH 4.7 are purely repulsive on approach and retract, in contrast to direct adsorption at pH 5.0. This demonstrates how adsorption hysteresis and non-equilibrium layer conformations can strongly influence surface forces and provide access to non-trivial interaction forces.

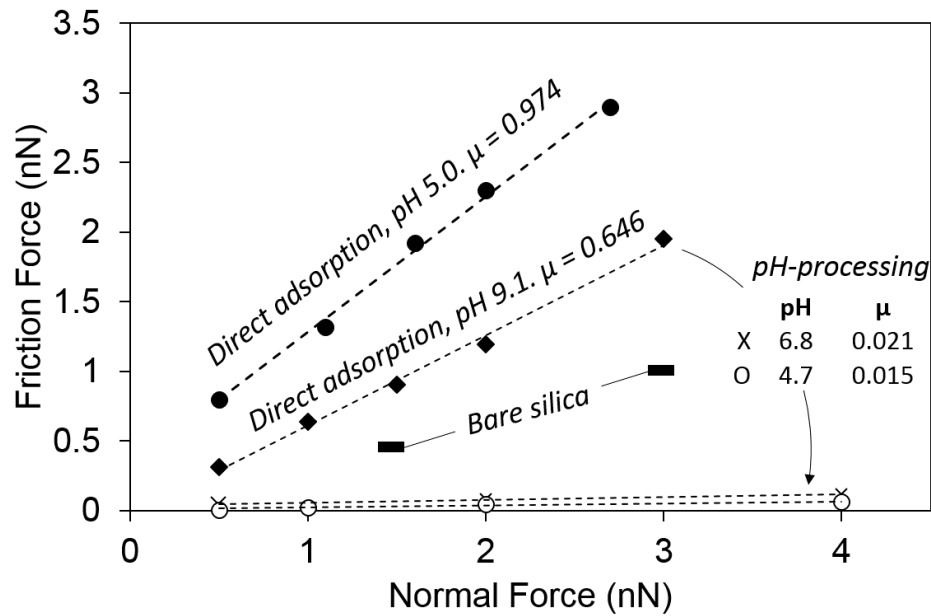


Figure 5.4. Friction measurements between a 20 μm silica colloidal probe and a flat silica substrate across 10 mM NaCl. Bare surface friction at pH 9.2 (bars), and SiO₂-*g*-PDMAEMA coated surfaces directly adsorbed to pH 5.0 (filled circles) and pH 9.1 (filled diamonds). pH-processed layers by rinsing the pH 9.1 adsorbed layer to pH 6.8 (crosses) and pH 4.7 (circles). The nature of the $F_N(D)$ profile for each friction curve can be seen in Figure 5.3.

Some of the friction properties of the SiO₂-*g*-PDMAEMA adsorbed layers, discussed above, are given in **Figure 5.4**. Comparisons between directly adsorbed and pH-processed layers are shown, including coefficient of friction values. The correlation between the nature of the normal force profiles – repulsive or adhesive – and the resulting frictional characteristics are clear. Directly-adsorbed layer that display attractive interactions in normal force profiles also display higher coefficients of friction. Direct adsorption at pH 5.0 had a larger adhesive force and larger coefficient of friction than is observed for direct adsorption at pH 9.1. The resulting coefficients of friction are higher than that observed for bare silica surfaces, indicating the modification of the surfaces with an adhesive coating. However, when the directly adsorbed pH 9.1 layer is rinse to pH 6.8 and pH 4.7, the coefficient of friction drastically reduces. For instance, an almost two order of magnitude reduction in friction coefficient is observed when comparing directly adsorbed SiO₂-*g*-PDMAEMA at pH 5.0 and pH processed SiO₂-*g*-PDMAEMA at pH 4.7. This again is tied to the nature of the normal force interactions, where purely repulsive, non-adhesive interactions were observed after pH-processing. It is also important that the friction coefficient is substantially lower than that of bare silica. The ability to switch friction and adhesion between silica surfaces is clearly feasible using SiO₂-*g*-PDMAEMA adsorbed layers. The measured coefficients of friction of ~ 0.02 , after charging and swelling of the particles through pH-processing, are comparable to friction coefficients measured between planar PDMAEMA brushes at low pH⁴ and other dense, polyelectrolyte brushes⁵. This suggests that SiO₂-*g*-PDMAEMA can behavior qualitatively similar to

planar brushes, but have the added ability to modulate their coverage by brush swelling and de-swelling in the direction parallel to the surface.

Adhesion and friction are generally correlated in tribological systems, and the following model relating the two was proposed by Derjaguin⁶:

$$F_F = \mu F_n + F_{f,0} \quad (5.1)$$

This prediction accounts for intermolecular adhesive forces by an inherent, zero-load friction force, $F_{f,0}$. We have observed this type of linear behavior in the friction versus load curves displayed throughout, for example in **Figure 5.4**. The nature of the friction coefficient will depend on surface topography, brush properties, and dynamic layer properties, thus making it difficult to predict qualitatively or quantitatively. However, if we assume that the adhesive forces are dominated by SiO₂-*g*-PDMAEMA bridging across surfaces, we can make simple arguments to predict adhesion thresholds. Adhesion between the surfaces is expected to a first approximation when the average space between adsorbed particles is greater than the particle diameter. This would allow, on average, a number of adsorbed particles to bridge across surfaces without significant steric and electrostatic repulsions preventing the bridge formation. Here, we will represent the space between adsorbed particles as the average edge-to-edge distance between particles, $\bar{d}_{edge}$, which can be related to the size of the particles and the number of adsorbed particles by the following:

$$\bar{d}_{edge} = \bar{d}_{center} - 2R_{p,excl}$$

$$\bar{d}_{center} = \Gamma^{-1/2} \quad (5.2 - 4)$$

$$R_{p,excl} \approx R_h + \kappa^{-1}$$

where Γ is the number density of particles on the surface and $R_{p,excl}$ is the radius of the circle that the adsorbed particle occupies on the surface. $R_{p,excl}$ includes contributions from the physical size of the particle, estimated by the hydrodynamic radius R_h and the Debye length κ^{-1} , or characteristic length scale for electrostatic potential decay away from the charged particles. $R_{p,excl}$ and Γ both depend on pH and salt concentration and are experimentally accessible. Comparison of the edge-to-edge distance expected for adsorbed SiO₂-g-PDMAEMA layers and the particle size leads to an expected adhesion threshold at the condition $\bar{d}_{edge} = 2R_{p,excl}$, or the dimensionless particle spacing criterion:

$$\frac{\Gamma^{-1/2}}{2(R_h + \kappa^{-1})} - 1 \begin{cases} > 1, \text{adhesive} \\ < 1, \text{repulsive} \end{cases} \quad (5.6)$$

In the case of the force and friction measurements in **Figure 5.3** and **Figure 5.4** the ionic strength is 10 mM NaCl, and $\kappa^{-1} = 3$ nm. The measured hydrodynamic radius as a function of pH is shown previously in **Figure 4.1**. Particle coverage is measured via AFM following each experiment. The comparison of experimental force curves with Equation 5.6 is shown in **Figure 5.5**, and excellent agreement is found for predictions of whether the force profiles should be adhesive or repulsive. Equation 5.6 is in agreement with experiments for both direct adsorption and pH processing experiments. This is merely a coarse assessment of

the adhesive interactions, but the ability to predict simply whether a layer is adhesive or repulsive is useful for identifying conditions that will likely result in relatively low or high friction. Given the large parameter space (pH, salt, coverage, hysteresis) that can be used to manipulate adsorbed layer conformation, these predictions can be used to preemptively screen conditions and aid in experimental design. This analysis could be made semi-quantitative by including electrostatic interactions that account for the charges of the particles and the silica surface. This analysis would also need to be modified if the particles exhibited non-random ordering on the surface, and the average particle spacing would no longer be sufficient to describe the accessible surface area.

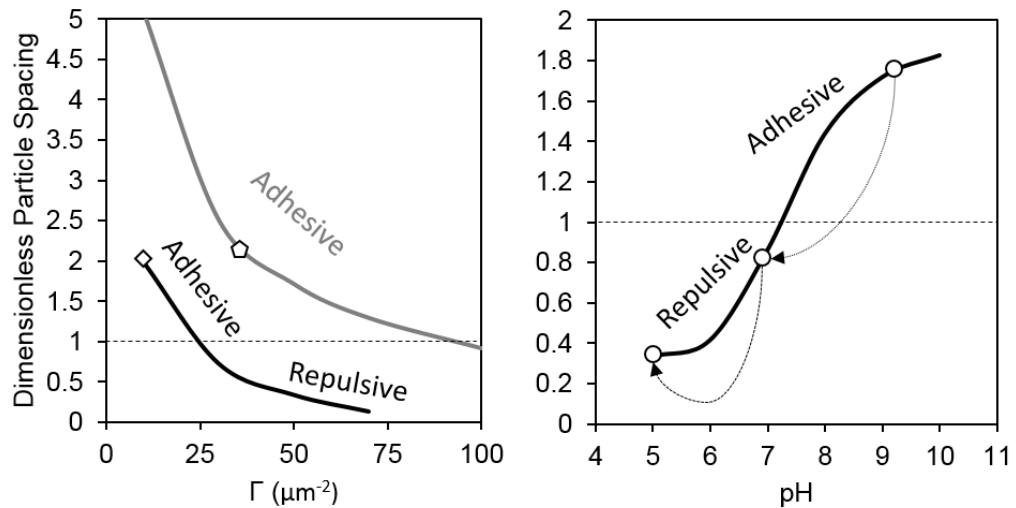


Figure 5.5. Comparison of experimental normal force profiles with predictions for the adhesion threshold based on Equation 5.6. Above a spacing of 1, the forces are expected to be adhesive. Below 1, the forces are expected to be repulsive. *Left:* Spacing as a function of particle density at pH 5.0 (black line) and pH 9.0 (grey line). Experimental forces curves for direct adsorption are shown as data points. pH 5.0 (diamond) and pH 9.1 (pentagon). *Right:* Spacing as a function of pH for $\Gamma = 35/\mu\text{m}^2$. Data points (circles) correspond to pH processing experiments with initial adsorption at pH 9.1 and rinses to pH 6.8 and pH 4.7.

5.2.2 *Reversible switching of adhesion and friction*

Adhesion and friction switching using pH effects is further illustrated in **Figure 5.6** and **Figure 5.7**. Here, adsorption of SiO₂-*g*-PDMAEMA involves the adsorption of larger, multi-particle aggregates from suspension. The aggregates are identified in DLS measurements, where the average aggregate size is 500 nm with very large polydispersity. Aggregation can be present in suspensions if the SiO₂-*g*-PDMAEMA particles have not been fully dispersed when going from the dry SiO₂-*g*-PDMAEMA powder to aqueous suspensions of particles. This process usually involves multiple sonication cycles while constantly maintaining the pH in acidic conditions. Eventually aggregates will break up and SiO₂-*g*-PDMAEMA fully dispersed into individual particles. However, insufficient sonication and pH conditioning during work-up will result in a polydisperse suspension of large aggregates. It is instructive in practice to study these imperfect suspensions and whether adsorbed aggregates can mediate friction similar to single-particle adsorbed layers, since it may be possible to reduce energy-intensive particle dispersion process for larger scale suspension formulation.

The presence of larger, multi-particle aggregates on the surface is evident in the normal force profiles of **Figure 5.6**. After adsorption from the polydisperse suspension, attractive forces persist during pull-off at distances up to 1 – 2 microns at pH 8.75. The adhesion curve features multiple pull-off events indicative of “strands” of particles bridging across the surfaces. These strands can either break during extension or desorb from the surface, and both bridging and interparticle interactions contribute to the overall adhesion. However, these long

range attractions are made significantly shorter range after compressing and shearing the layer in a friction measurement. This suggests that some of the loosely-bound aggregates are broken up via shear stresses applied on the layer. The post-friction force curves still display adhesive forces, but these only have a range of approximately 500 – 600 nm. Upon rinsing the aggregate layers to pH 5.2, the adhesive forces are no longer observed and purely repulsive normal forces are observed. This again is due to brush charging and swelling that occurs in response to the decreasing pH. These repulsions persist after compression and shear, indicating that little to no layer damage occurs. This is in contrast to the shear-induced change in layer conformation at pH 8.75. Repulsive interactions on approach are shown on a *log-lin* plot, and the particle layers display longer range interactions than are observed for well-dispersed, single particle layers such as those in **Figure 5.3**.

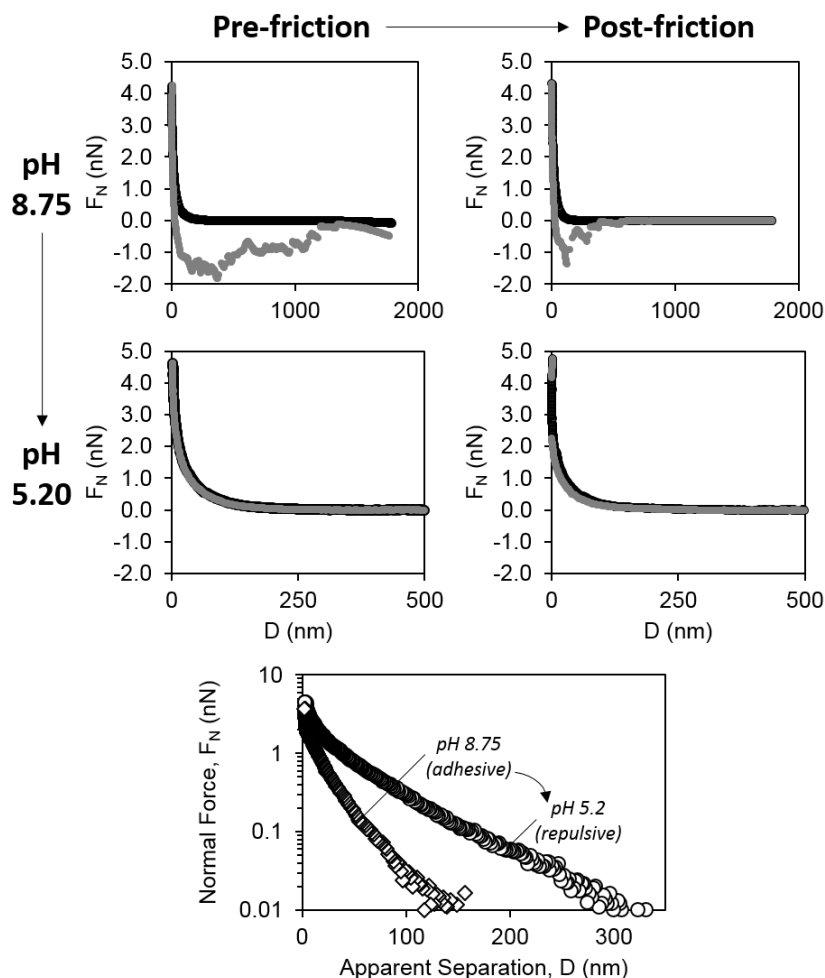


Figure 5.6. Adhesion switching between a 20 μm silica colloidal probe and a flat silica surface, both bearing adsorbed SiO_2 - g -PDMAEMA “aggregate” layers. Normal force profiles are shown before and after subjection to compression and shear in friction versus load experiments detailed in **Figure 5.7**. *Top row:* pH 8.75, displaying long-range bridging forces before friction, and substantially shorter range bridging forces after friction. *Middle row:* Rinsing to pH 5.20. Uniform repulsions before and after friction. *Bottom row:* Approach curves showing the extended range of repulsions after swelling and charging the adsorbed layers. Note: differences in x -axis scale.

Friction forces between the aggregate coated surfaces are shown in **Figure 5.7**. Switchable friction behavior upon rinsing from pH 8.75 to pH 5.20 occurs and correlates with the nature of the observed normal force profiles – adhesion with higher friction and repulsions with lower friction. Here, friction switching is

observed over two swelling and de-swelling cycles. The measured friction coefficients are higher for the aggregate layers than for the single-particle layers shown earlier, likely due to the enhanced roughness of these layers. The zero-load friction for the adhesive aggregate layers (pH 8.75) are approximately 4 – 5 times higher than the single particle layers in **Figure 5.3** owing to the larger energy dissipation caused by the longer-range bridging adhesion for the aggregates.

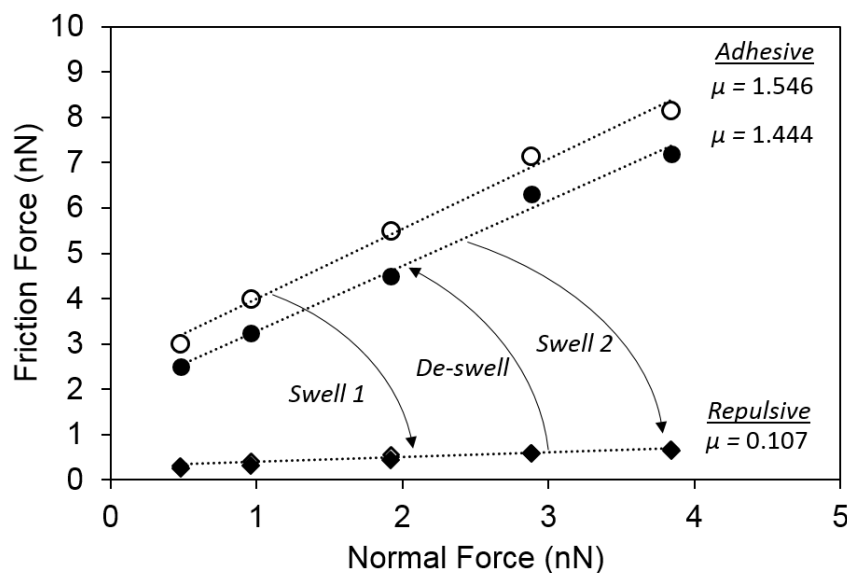


Figure 5.7. Friction switching by pH-induced swelling of adsorbed SiO₂-g-PDMAEMA “aggregate” layers across 10 mM NaCl. Sliding speed is 5 μm/s. Initially, the layer is formed at pH 8.75 (open circles), then rinsed to pH 5.20 (open diamonds), then rinsed back to pH 8.75 (closed circles), and again to pH 5.20 (closed diamonds). The open and closed diamonds overlap. Note: the normal force profiles – adhesive or repulsive – are shown in **Figure 5.6**.

5.2.3 Coverage effects on surface forces

The previous section discusses direct adsorption and pH-processing routes to control friction and adhesion between *symmetric* adsorbed layers of SiO₂-g-PDMAEMA. This method can only coarsely assess the effects of coverage on bridging attraction and other interactions. The experiment in **Figure 5.7** highlights

coverage effects by utilizing *asymmetric* adsorbed SiO₂-*g*-PDMAEMA layers. Here, the flat silica substrate is pre-coated with a high-coverage layer of SiO₂-*g*-PDMAEMA by adsorbing at pH 9.1 and elevated temperature of 40 °C. AFM images display a number density of ~ 250 particles per μm^2 , similar to images presented in **Figure 4.9**. The pre-coated substrate is mounted into the fluid cell and solvated by 10 mM NaCl at pH 5.0.

Colloidal probe measurements are initiated first using a bare probe against the high-coverage SiO₂-*g*-PDMAEMA layer. Here, purely attractive forces are observed on approach of the surfaces. This is strongly indicative of traditional bridging interactions, where SiO₂-*g*-PDMAEMA adsorbed on the surface “grab” the opposing bare silica probe. The onset of interactions should correspond to a characteristic length scale for the bridging entity⁷ – in this case, the SiO₂-*g*-PDMAEMA particle diameter. Attractive forces arise at an apparent separation distance of ~ 90 nm, in good agreement with the expected swollen dimensions of the particles in 10 mM NaCl, pH 5.0. The separations are not absolute distances so this value should not be over-interpreted. A large adhesive force is observed upon retraction and pull-off of the probe from the surface, further confirming the presence of a high coverage adsorbed layer on the surface. It is important to note that the interactions do not seem to change upon repeated approach and retraction of the surfaces, suggesting that little to no SiO₂-*g*-PDMAEMA transfers from the surface to the probe due to compression and extension of the particle adsorbed layer. It is likely that the adsorbed particles are more strongly adsorbed to the flat silica surface than they are to the probe upon dynamic bridging, since SiO₂-*g*-

PDMAEMA is adsorbed in the collapsed state and then re-solvated, ensuring a large number of monomers contact and remain trapped near the surface.

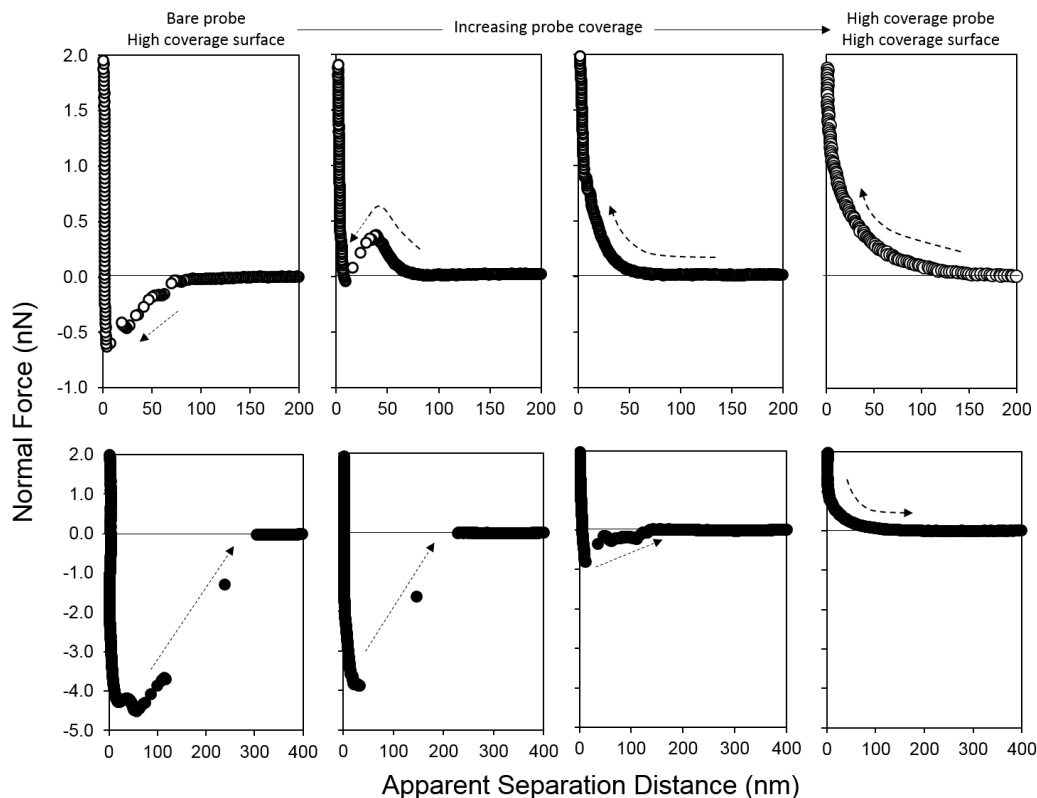


Figure 5.8. Force curves between a 20 μm silica colloidal probe and a flat silica surface with asymmetric surface coverages of $\text{SiO}_2\text{-}g\text{-PDMAEMA}$, across 10 mM NaCl background electrolyte. *Left:* Bare probe against a high-coverage surface formed by temperature driven adsorption near the CFT. *Middle Left:* probe with low coverage of $\text{SiO}_2\text{-}g\text{-PDMAEMA}$, achieved particle transfer after shearing the bare probe against the high-coverage surface. *Middle Right:* Higher coverage probe, achieved by introducing a $\text{SiO}_2\text{-}g\text{-PDMAEMA}$ suspension and allowing fresh nanoparticles to adsorb to the probe. *Far Right:* Separate experiment where temperature-driven high coverage layers are formed on both the surface and the probe prior to mounting in the flow cell. Note: different force and distance scales for the approach and retract curves.

The force curves develop repulsive features on approach upon the addition of $\text{SiO}_2\text{-}g\text{-PDMAEMA}$ to the bare silica probe counter-surface. The middle left plot in **Figure 5.8** represents the post-friction force curves between the bare probe

and the high-coverage adsorbed layer. SiO₂-*g*-PDMAEMA particles transfer to the probe after compression and shear of the layers. Particle transfer during compression and shear is in contrast to pure compression, which resulted in reversible force curves with the same purely repulsive bridging attraction over multiple approach and retract cycles. This observation indicates that the adsorbed SiO₂-*g*-PDMAEMA are more susceptible to change their conformation in response to shear stress than elongational stresses. The sliding speed is 5 µm/s during friction measurements. Normal force measurements are performed at an approach and retract speed of 200 nm/s. The much faster rate of deformation of bridged particles during shear may contribute to desorption from the flat surface and re-adsorption onto the opposing silica probe. The normal forces on approach between the low coverage probe and high coverage surface confirm the presence of SiO₂-*g*-PDMAEMA, as both repulsive and attractive forces are measured. Repulsion between the surfaces occurs first followed by a snap in attraction. The repulsions are caused by overlap of particles on the opposing surface. However, due to the low number of adsorbed SiO₂-*g*-PDMAEMA on the probe, the repulsions give way to bridging attraction once the high-coverage layer is driven past the protruding particles. Strong adhesion is again observed on retraction owing to the strong coverage asymmetry. The maximum adhesion is slightly lower than the high-coverage/bare probe measurement. This can be attributed to the slightly reduced area available for bridging now that the probe bears adsorbed particles.

A further increase in coverage on the probe side is achieved by adsorbing fresh SiO₂-*g*-PDMAEMA from suspension. This occurs via direct adsorption and the expected layer coverage will still be sub-monolayer. The force curves on approach between the intermediate and high-coverage layers are now purely repulsive. The disappearance of attractive features that were observed for lower coverage adsorbed layers indicates the successful incorporation of more particles on the probe surface. The interactions here also suggest that jump-in of the surfaces can be prevented with sufficient surface coverage. This type of layer would be resistant to bridging unless forced into confinement and close contact. Significantly reduced adhesive forces are experienced upon retraction of the surfaces. This again is tied to the reduced surface area available for bridging on the probe. Friction loops corresponding to these conditions are shown in **Figure 5.9**. Substantial friction is measured for the strong bridging, purely asymmetric bare probe versus high coverage layer. Upon addition of a medium coverage adsorbed layer, friction is reduced by an order of magnitude. This is largely due to the reduced bridging adhesion and energy dissipation via breaking the bridging segments. It is notable that the lateral sticking events are approximately the same spatial distance, indicating that in fact the layer is undergoing constant bridge formation and breakage.

Finally, an interactions are measured in an independent experiment where high-coverage SiO₂-*g*-PDMAEMA layers are formed on both the probe and surface via temperature driven adsorption near the CFT, followed by re-solvation in the AFM fluid cell. Here, coverage symmetry and little exposed silica on either

surface leads to pure repulsions on approach and no adhesion on retraction.

Repulsions are much longer range for the conformal SiO_2 -*g*-PDMAEMA coated surfaces than were observed for the asymmetric coated surfaces. These experiments highlight the importance of surface coverage on the adhesive interactions resulting from SiO_2 -*g*-PDMAEMA adsorbed layers. Importantly, different bridging regimes are identified based on coverage asymmetry – spontaneous bridging, weak electrosteric hindrance to bridging, strong electrosteric hindrance to bridging, and full prevention of bridging.

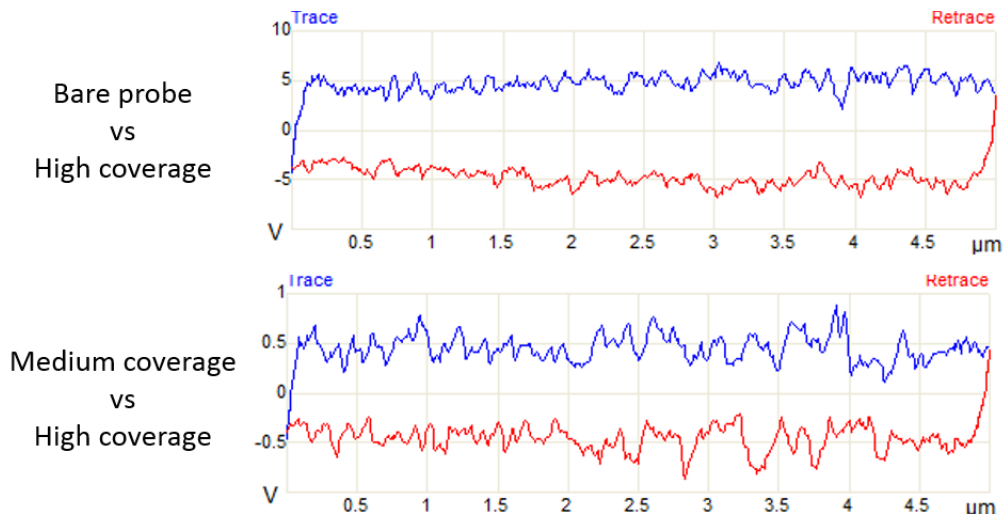


Figure 5.9. Friction traces between a 20 μm silica colloidal probe and a flat silica surface with asymmetric surface coverages of SiO_2 -*g*-PDMAEMA, across 10 mM NaCl background electrolyte at an applied load of 3 nN. *Top*: friction loops corresponding to the first panel in Figure 5.8, with pure bridging. *Bottom*: friction loops corresponding to the third panel in Figure 5.8, with repulsions on approach and weak adhesion. Friction forces are reduced by an order of magnitude by addition of particles to the probe.

5.2.4 Stability of SiO_2 -*g*-PDMAEMA-coated latex microparticles

The force curves presented in the above sections are all obtained by driving brush nanoparticle coated surfaces together under strong applied loads.

This tribological method for evaluating surface forces is required for assessing the tenacity of lubricating layers operating in forced, close confinement. Observations of bridging adhesion are valid because the surfaces have been driven together in spite of repulsive interactions that can kinetically limit this adhesion from occurring. Thus, care must be taken in translating the interaction forces measured here and interaction forces that may be encountered in dilute to semi-dilute suspensions where interactions between brush nanoparticle-coated surfaces result from stochastic, Brownian motion-driven collisions. These systems are relevant in colloidal stability⁸ and dispersion processing applications where confinement is not imposed on the polymer brush nanoparticle coated surfaces.

An example of this is our group's extensive previous work on nanoparticulate polymer brush emulsifiers^{9,10}. SiO₂-*g*-PDMAEMA and star PEO both stabilize oil/water emulsions at low particle concentrations, indicating that these nanoparticulate brushes can adsorb to interfaces and provide strong barriers to coalescence of micron sized droplets. This dissertation is concerned with solid/liquid interfaces, so we have studied SiO₂-*g*-PDMAEMA as stabilizer for colloidal, polystyrene latex suspensions. This study was performed as a part of the Masters' Thesis of Bhagyashree Lele¹¹, but was directly supervised under the author of this dissertation. The studies here utilized optical density, or turbidity, methods to assess the stability of negatively charged sulfonated polystyrene latex (S-PSL) microparticle suspensions with varying salt and SiO₂-*g*-PDMAEMA concentrations.

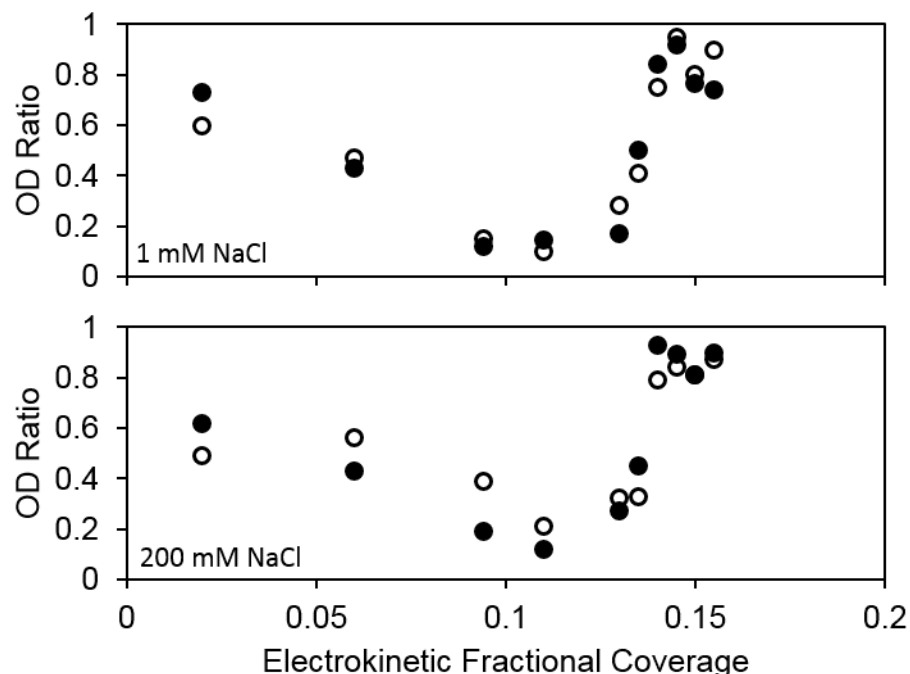


Figure 5.10. Turbidity of suspensions containing negatively charged, 1 μm sulfonated polystyrene latex microparticles and adsorbing SiO_2 -*g*-PDMAEMA. The optical density is measured at 600 nm. Measurements at pH 5.0 (open circles) and pH 9.0 (closed circles). The x-axis is determined from zeta potential measurements of the SiO_2 -*g*-PDMAEMA coated latex particles and the surface coverage extracted using the Adamczyk electrokinetic model¹². Fractional coverage increases with increasing SiO_2 -*g*-PDMAEMA bulk concentration. Bridging flocculation is observed at low to intermediate coverages, and stabilization occurs as the coverage reaches 0.14 to 0.16. The OD ratio is 1 with zero adsorbed SiO_2 -*g*-PDMAEMA.

Figure 5.10 shows an example of the suspension stability of S-PSL as a function of the approximate surface coverage of SiO_2 -*g*-PDMAEMA. Changes in the optical density (OD) of the suspension correspond to relative changes in stability. Suspension de-stabilization results in S-PSL aggregation and sedimentation, manifesting as a decrease in OD. The surface coverage is estimated from zeta potential measurements of the SiO_2 -*g*-PDMAEMA-coated S-PSL particles. Coverage can be extracted from the coated particle zeta potential

using an analytical model derived by Adamczyk model¹³ based on the pure SiO₂-*g*-PDMAEMA and S-PSL zeta potentials. This provides a calibration curve for coverage of SiO₂-*g*-PDMAEMA on S-PSL as a function of bulk SiO₂-*g*-PDMAEMA concentration. Thus, OD vs. SiO₂-*g*-PDMAEMA concentration data can be indirectly converted to OD vs. apparent electrokinetic coverage data as plotted in **Figure 5.10**. The data exhibits typical features associated with stability of a colloidal suspension of a charged particle in the presence of an oppositely charged, adsorbing polyelectrolyte¹⁴. The decrease in stability during initial SiO₂-*g*-PDMAEMA adsorption is caused by a combination of reduced net surface charge and bridging interactions. The suspension then becomes more stable as the apparent surface coverage reaches approximately 10 – 15%. Here, electrosteric interactions become sufficient to overcome attractive van der Waals interactions and increase S-PSL stability. The OD levels off at a surface coverage of 16%, where the surface charge reaches saturation. This suggests that significantly sub-monolayer coverages - well below RSA (55%) or HCP (74%) packing limits - provide sufficient repulsive interactions to kinetically limit aggregation of the S-PSL.

The situation encountered here involves *direct adsorption* of SiO₂-*g*-PDMAEMA, and thus the force curves at pH 5.0 and pH 9.0 in **Figure 5.3** are likely representative of the interactions as a function of separation. Although bridging interactions are observed for these sub-monolayer coverages, repulsive interactions are always measured on approach of the surfaces. Bridging attraction is enabled because the surfaces are forced over this repulsive barrier. In a dilute

suspension subjected to Brownian motion, this barrier is sufficient to kinetically limit bridging from occurring. This supports the observation that sub-monolayer coverages can impart repulsions and not necessarily induce bridging flocculation. This effect of low-coverage stabilization has been observed for highly-charged zirconia nanoparticles on silica microparticles¹⁵. This could impart interesting rheological properties upon suspensions of SiO₂-*g*-PDMAEMA coated microparticles, where shear forces impart higher collision frequencies and local kinetic energy to interacting suspension particles¹⁶. This may result in different, tunable shear-thickening properties¹⁷ than have been previously observed for brush-coated nanoparticles.

5.3 Conclusions

The interactions between negatively charged surfaces bearing adsorbed non-ionic and cationic polymer brush nanoparticles have been assessed primarily using colloidal probe force measurements. Insights from detailed adsorbed layer characterization in previous chapters guide the interpretation of force vs. distance and friction vs. load curves presented here. Star PEO impart purely repulsive forces on silica surfaces that further suggest the formation of a dense, brush-like adsorbed layer. Modest friction coefficients of approximately 0.15, coupled with PEO's well known biocompatibility, indicate their potential as boundary lubricants.

SiO₂-*g*-PDMAEMA exhibits adhesive bridging interactions that can be tuned via hysteretic adsorption effects and pH changes to impart switchable friction behavior to silica surfaces. This behavior is controlled by pH-induced

surface swelling of the SiO₂-*g*-PDMAEMA particles that modulates the inter-particle spacing and area of surface accessible for bridging. Larger surface aggregates also display this behavior, indicating that well defined swelling and collapse of SiO₂-*g*-PDMAEMA is not required for tunable friction properties. A broad range of friction coefficients $\sim 0.01 - 1.5$ were achievable using symmetric adsorbed layers. Finally, coverage-dependent bridging interactions are elucidated via asymmetric force measurements and suspension stability analysis. The nature of particle-induced barriers to bridging adhesion are important when considering the degree of confinement under which the adsorbed layers will be studied. The coupled effects of coverage and pH ultimately play a crucial role in determining the adhesive and frictional properties of SiO₂-*g*-PDMAEMA adsorbed layers. It is evident from the studies here that SiO₂-*g*-PDMAEMA layers show promising responsive film properties for friction control.

5.4 References

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6. Ionic surfactant binding to pH-responsive polyelectrolyte brush-grafted nanoparticles in suspension and on charged surfaces

The interactions between silica nanoparticles grafted with a brush of cationic poly(2-(dimethylamino) ethyl methacrylate) (SiO_2 -*g*-PDMAEMA) and anionic surfactant sodium dodecyl sulfate (SDS) is investigated by dynamic light scattering, quartz crystal microbalance with dissipation, ellipsometry, and atomic force microscopy. SiO_2 -*g*-PDMAEMA exhibits pH-dependent charge and size properties which enables SDS binding to be probed over a range of electrostatic conditions and brush conformations. SDS monomers bind irreversibly to SiO_2 -*g*-PDMAEMA at low surfactant concentrations ($\sim 10^{-4}$ M) while exhibiting a pH-dependent threshold above which cooperative, partially reversible SDS binding occurs. At pH 5, SDS binding induces collapse of the highly charged and swollen brush as observed in the bulk by DLS and on surfaces by QCM-D. Similar experiments at pH 9 suggest that SDS binds to the periphery of the weakly charged and de-swollen brush and produces SiO_2 -*g*-PDMAEMA/SDS complexes with a net negative charge. Hydrophobic effects likely play a role in the surfactant binding and contribute a non-electrostatic driving force for binding. SiO_2 -*g*-PDMAEMA brush collapse and charge neutralization is further confirmed by colloidal probe AFM measurements, where reduced electrostatic repulsions and bridging adhesion are attributed effects of the bound SDS. Additionally, sequential adsorption schemes with SDS and SiO_2 -*g*-PDMAEMA are used to enhance deposition relative to SiO_2 -*g*-PDMAEMA direct adsorption on silica.

6.1 Introduction

Branched polymeric nanostructures such as dendrimers^{1,2}, star polymers^{3,4}, bottle-brush polymers^{5,6}, and polymer-grafted nanoparticles⁷ are emerging as promising surface active materials and understanding their interaction with traditional small molecule surfactants is important for their employment in technologically relevant surface conditioning formulations^{8,9}. Many of these polymers and polymeric nanomaterials have amphiphilic as well as polyelectrolyte components that will interact with oppositely charged surfactants through electrostatic and hydrophobic interactions, driving surfactants to bind along the polymer chains at concentrations often lower than their critical micelle concentration in solution¹⁰. Ionic surfactants exhibit two primary modes of binding to polyelectrolytes: stoichiometric binding of surfactants to oppositely charged groups on the polyelectrolyte and cooperative binding to form self-assembled polyelectrolyte/surfactant complexes.

Polyelectrolyte/surfactant complexes commonly exhibit modified bulk and interfacial properties from their single component counterparts¹¹. Much work has been done investigating adsorption mechanisms, layer structure, and forces between surface-bound polyelectrolyte/surfactant mixed layers¹²⁻¹⁴, which frequently persist in non-equilibrium conformations¹⁵⁻¹⁸. Such layers are sensitive to the layer formation pathway, and the pathway must be carefully specified when interpreting these systems. Despite the complex adsorption mechanism, many of the same polyelectrolyte/surfactant complexation features that arise in the bulk solution are consistent with findings when the complexes

form at a surface. Previous work in the field has focused mainly on the interactions between linear polyelectrolytes, block co-polymers, grafted polymers and bottle-brush polymers with oppositely charged surfactants both in the bulk and at interfaces or surfaces^{12,19–21}.

This study concerns complexation and adsorption at the solid/liquid interface. A system of oppositely charged surfactants and macromolecules and a surface that is selective for adsorption of only one component (often the macromolecule, as is the case in the current investigation) and repellant to the other is categorized as Type I co-adsorption system^{11,22} and is representative of many commercial surface conditioning applications. Arteta and coworkers²³ investigated the co-adsorption of 2-7 nm diameter cationic poly(amido amine) (PAMAM) dendrimers and anionic sodium dodecyl sulfate (SDS) at the negatively charged silica/water interface. Although a fundamentally different class of polymeric material, dendrimers have some features in common with BGNPs. Using quartz crystal microbalance with dissipation (QCM-D) and neutron reflectivity, Arteta and coworkers found that surfactants bind individually to pre-adsorbed PAMAM dendrimers at low surfactant concentrations and bind cooperatively to form self-assembled, adsorbed complexes at higher surfactant concentrations. Persistent non-equilibrium states were produced, whereby sequential or simultaneous co-adsorption pathways produced different mixed layer structures.

Here we study complexation of SDS with cationic BGNPs consisting of a 15 nm diameter silica core and a grafted brush of the weak polyelectrolyte poly(2-

(dimethylamino) ethyl methacrylate), (SiO_2 -*g*-PDMAEMA BGNPs). The weak polycation BGNPs have pH dependent size and net charge, as the polyelectrolyte degree of protonation depends on pH and ionic strength. With a weak polycation, differences in surfactant binding behavior are expected when comparing complexation and co-adsorption under strongly charged and stretched brush conditions (low pH) and weakly charged and relatively collapsed brush conditions (high pH). First, we use a combination of dynamic and electrophoretic light scattering to monitor SDS binding to SiO_2 -*g*-PDMAEMA BGNPs and its effects on brush charge and swelling in suspension. Next, adsorption and formation of mixed surfactant/BGNP layers on negatively charged silica surfaces is investigated with a combination of QCM-D, ellipsometry, and atomic force microscopy. Both sequential adsorption of BGNPs and SDS and co-adsorption from mixtures are considered. Finally, colloidal probe AFM force measurements and simultaneous QCM-D/ellipsometry measurements test the influence of bound SDS on surface forces and swelling dynamics, highlighting practically useful interfacial properties that can be controlled by processing surface adsorbed polyelectrolyte BGNP layers with surfactant.

6.2 Complexation of SiO_2 -*g*-PDMAEMA and SDS in bulk suspension

6.2.1 Particle Size and Charge

The hydrodynamic diameter and electrophoretic mobility of SiO_2 -*g*-PDMAEMA BGNPs in the presence of SDS are shown in Figure 6.1 for pH 5 and pH 9 at a fixed NaCl concentration of 10 mM. The nanoparticle concentration was 0.1 mg/mL. The size and mobility of the BGNPs are controlled by the pH and

ionic strength of the electrolyte reservoir, as these determine the degree of protonation of dimethyl amine groups ($pK_a \sim 7.0-7.5$) and also the length scale for electrostatic interactions that control brush swelling. Using the planar ionizable brush theory of Zhulina and coworkers,²⁴ we estimate the degree of PDMAEMA protonation as 0.86 ± 0.02 at pH 5 and 0.07 ± 0.03 at pH 9 for the grafting density and average brush thickness of the current BGNPs and a pK_a of 7.2. It should be noted that the degree of protonation will vary with depth in these spherical brushes due to a segment density profile that decays more rapidly than in a planar brush with increasing distance from the grafting site/core,²⁵ but it is apparent from **Figure 6.1** that the degree of protonation varies greatly between pH 5 and 9. The BGNPs have an apparent zeta potential of +55 mV at pH 5 in 10 mM NaCl in the absence of SDS. The large degree of protonation at pH 5 results in a brush that is relatively extended. The brush thickness calculated from the hydrodynamic radius of the grafted particle by subtracting the average radius of the silica cores is approximately 28 nm, close to the contour length of the PDMAEMA chain $L_c = n_{DMAEMA}a_{DMAEMA} = 33$ nm. At pH 9 the apparent zeta potential of the particles is +12 mV, significantly lower than at pH 5. The low charge collapses the brush to a thickness of approximately 10 nm, nearly 3-fold less extended than at pH 5 in the absence of SDS.

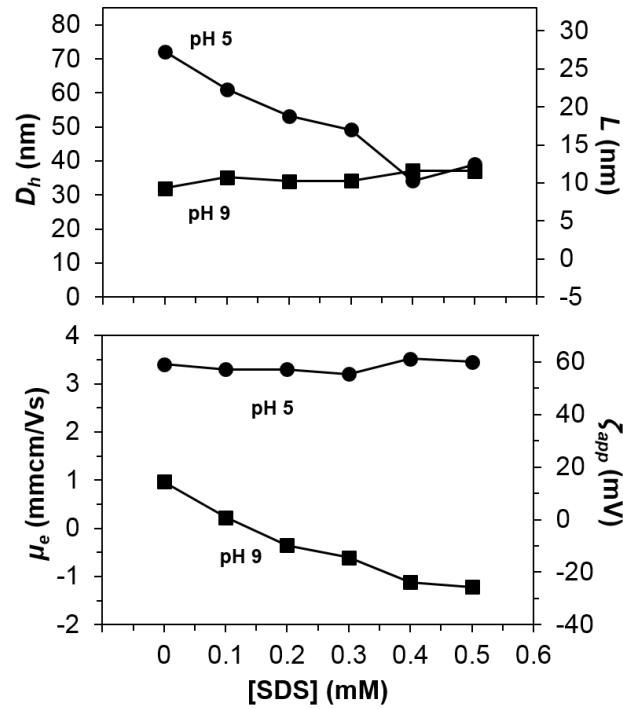


Figure 6.1. Particle size and electrophoretic mobility of SiO₂-*g*-PDMAEMA/SDS complexes in acidic (circles) and basic (squares) pH conditions. The brush thickness $L = (D_h - D_{core})/2$ is shown in the top plot. The apparent zeta potential $\zeta = \mu\eta/\epsilon_r\epsilon_0f(\kappa R_h)$ is shown in the bottom plot. Binding of SDS to the nanoparticles is indicated by brush collapse at low pH and by a reversal of mobility at high pH.

The hydrodynamic diameter and electrophoretic mobility indicate binding of SDS to the BGNPs at both pH 5 and 9, but the evidence manifests itself differently for each pH. As we add SDS to a pH 5 dispersion we observe significant decreases in hydrodynamic diameter with increasing SDS concentration, indicating increasing brush collapse. This is due to the weakening of electrostatic repulsions that occurs as anionic surfactants bind to cationic groups in the brush. At 0.5 mM SDS, the brush/surfactant corona thickness is similar to the surfactant-free SiO₂-*g*-PDMAEMA corona in its weakly charged state at pH 9. Despite clear evidence for SDS binding at pH 5, the electrophoretic

mobility remains relatively constant and positive up to 0.5 mM SDS. This counterintuitive result that the electrophoretic mobility would remain constant upon binding of SDS is explained by the simultaneous decrease in both the number of charges and the thickness of the brush, as supported by numerical calculations of the Hill and Saville model²⁶ for electrophoresis of polymer-coated colloidal particles. Details are provided in Supporting Information. Input parameters to the model include the hydrodynamic radius, number of charges, ionic strength, and estimations of the Brinkman screening length. By assuming 1:1 charge neutralization between SDS molecules and DMAEMA monomers and correcting the permeability (Brinkman screening length) of the polymer brush to account for additional volume occupied by SDS within the brush, the model predicts a mobility of $3.6 \mu\text{m cm V}^{-1}\text{s}^{-1}$ for the SiO_2 -*g*-PDMAEMA BGNPs in the absence of SDS in 10 mM NaCl at pH 5, and a mobility of $3.4 \mu\text{m cm V}^{-1}\text{s}^{-1}$ at 0.4 mM added SDS (~4500 SDS molecules bound/BGNP) at the same NaCl concentration and pH. These are both within one standard deviation of the experimental data. The relatively constant electrophoretic mobility results from mutually compensating effects of SDS binding (reduction of net positive charge) and brush thickness reduction that keep the net charge density in the brush relatively constant.

SDS binding at pH 5 decreased the hydrodynamic diameter and left the electrophoretic mobility nearly constant, whereas SDS binding at pH 9 caused a small increase in hydrodynamic diameter and strongly affected the electrophoretic mobility, driving it from positive to negative values. Unlike pH 5 where the brush

was highly stretched, it was already collapsed at pH 9 in the absence of SDS. Upon SDS addition at pH 9, the brush slightly swells. The increase in hydrodynamic diameter of less than 5 nm is consistent with adsorption of SDS on the brush periphery, as if it were a surfactant layer adsorbing to an impenetrable surface. The electrophoretic mobility decreased upon SDS addition, and a net reversal of sign occurred at 0.2 mM SDS. Further increases in SDS concentration caused the mobility to become more negative, reaching an apparent zeta potential of -25 mV at 0.5 mM SDS. Although the detailed distribution of SDS in the brush is not known, the trends of a large reversal of electrophoretic mobility with a modest size increase suggest peripheral SDS adsorption without significant penetration into the bulk of the brush. The monotonic decrease in electrophoretic mobility caused by SDS binding at high pH is consistent with mobility measurements of higher grafting density SiO₂-*g*-PDMAEMA BGNPs with SDS reported by our group previously²⁷, where deep surfactant penetration into the high density brush was sterically hindered. A reversal of zeta potential with added SDS was also observed for PAMAM dendrimers by Arteta and co-workers²³.

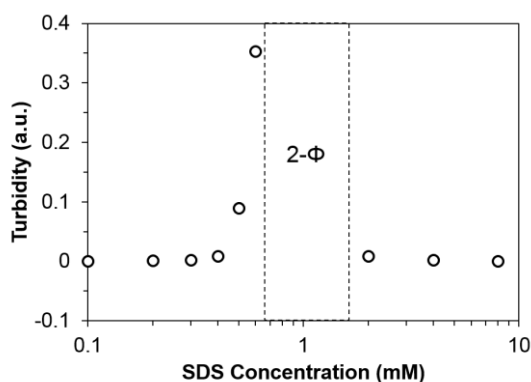


Figure 6.2. Turbidity measurements indicating SDS binding to 1.0 mg/mL SiO₂-*g*-PDMAEMA dispersion at 10 mM, pH 5.0. The two phase region of particle aggregation occurs from 0.6 – 1.6 mM added SDS.

Figure 6.2 shows the colloidal stability of a SiO₂-*g*-PDMAEMA suspension in the presence of added surfactant. The dispersed nanoparticles are at pH 5, and concentrated SDS is titrated into the suspension to produce surfactant concentration in the range 0.1 – 8.0 mM SDS. The SDS/ SiO₂-*g*-PDMAEMA mixture is stirred for 15 minutes and the optical density (turbidity) is recorded in a UV-Vis spectrophotometer at a wavelength of 508 nm. The SiO₂-*g*-PDMAEMA particles remain dispersed at low and high surfactant concentrations, corresponding to strongly positively and negatively charged particles respectively. Aggregation is observed beginning at 0.6 mM added SDS and the suspension remains cloudy with added SDS to 0.8, 1.0, 1.5 mM. The suspension becomes clear again after a total of 2.0 mM SDS is added. This stability behavior is typical of oppositely charged polyelectrolyte/surfactant systems, with the two-phase region corresponding to a region of weakened electrostatic repulsions.

6.3 Interaction of SDS and adsorbed brush-grafted nanoparticles

6.3.1 Swelling of adsorbed SiO₂-g-PDMAEMA with and without SDS

The results above demonstrated that SDS binds to BGNPs in the bulk and at pH 5 surfactant binding de-swelled the otherwise extended PDMAEMA brush of the BGNPs. It is also necessary to determine the extent with which bound SDS effects the dynamic swelling of BGNPs, in the event that SDS/BGNP complexes experience transient exposure to varying pH conditions. The following experiments, illustrated in **Figure 6.3**, directly test the pH responsiveness of brushes on BGNPs that are confined to the surface, and the ability of surface-

adsorbed BGNPs to swell in response to changes in pH both in the absence and presence of bound surfactant. Simultaneous QCM-D and ellipsometry is used to measure the frequency and dissipation shifts while also measuring the ellipticity of the adsorbed layer. The ellipsometry data is represented by the measured parameter γ , which generally represent changes in the optical thickness of an adsorbed layer. Here, ellipsometry provides an independent measure of the total adsorbed mass, with no contribution from trapped water, while the QCM-D dissipation shift can be used to track changes in the layer conformation relative to the initial bare surface state.

A description of the QCM-D/ellipsometry experiment and each step, represented by Roman numerals of **Figure 6.3** is detailed in the corresponding figure caption. Initially, SiO₂-*g*-PDMAEMA BGNPs are adsorbed on silica in a relatively collapsed state (pH 9.25). Upon rinsing the adsorbed BGNP layer with pH 9, slight swelling occurs at a constant adsorbed number of BGNPs. Subsequent rinses to pH 5, pH 9, and pH 5 show strong swelling, de-swelling, and re-swelling with only slight BGNP desorption on the initial pH 5 rinse due to strengthened lateral electrostatic repulsions. These results confirm that the brushes on adsorbed SiO₂-*g*-PDMAEMA BGNPs retain the reversible pH-responsiveness that they exhibit when dispersed in a bulk suspension. Abrupt changes in the dissipation signal due to swelling and de-swelling also have been observed for planar PDMAEMA brushes²⁸.

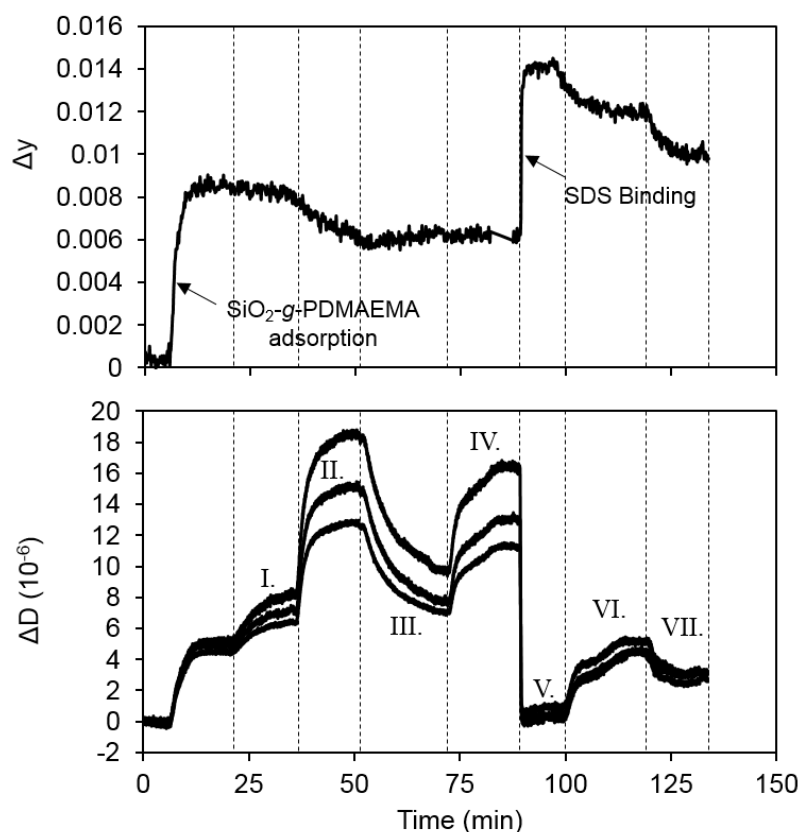


Figure 6.3. pH and surfactant induced swelling characteristics of adsorbed SiO₂-*g*-PDMAEMA monitored by simultaneous QCM-D/ellipsometry in 10 mM NaCl. *Top.* Ellipsometry signal, proportional to the adsorbed mass. *Bottom.* Concurrent QCM-D dissipation signal with swelling and de-swelling events indicated by the Roman numerals. I. weak swelling during rinse from pH 9.25 to pH 9.0. II. Strong swelling and desorption, rinse pH 9.0 to pH 5.0. III. De-swelling, rinse pH 5.0 to pH 9.0. IV. Re-swelling, rinse pH 9.0 to 5.0. V. Collapse and rigidification by addition of 1.0 mM SDS at pH 5.0. VI. Swelling by partial release of SDS during rinse at pH 5.0. VII. De-swelling, despite partial release of SDS, during rinse from pH 5.0 to 9.0.

Upon addition of 0.1 mM SDS, surfactant rapidly binds to the adsorbed BGNP layer (increase in y) and a very sharp layer collapse is observed in the dissipation signal dropping almost to zero. This layer collapse is more pronounced in magnitude and occurs more rapidly than the de-swelling that was induced upon changing from pH 5.0 to pH 9.0. The resulting BGNP/SDS layer is effectively

rigid, indicating that brush collapse is more effectively triggered by SDS complexation than pH-mediated intra-brush electrostatics. Rinsing the now complexed BGNP/SDS layer at pH 5.0 and then at pH 9.0 after surfactant binding shows much weaker dissipation response than the pure BGNPs had in the absence of SDS, indicating that the brush dynamics have been altered on the timescales of the pH modulation (~30 min). Hindered swelling behavior shows that of SiO₂-*g*-PDMAEMA and SDS are strongly complexed and that surfactant retention after rinsing strongly effects the brush dynamics.

6.3.2 *Effect of surfactant concentration on the binding of SDS to adsorbed SiO₂-*g*-PDMAEMA*

Since polyelectrolyte BGNP adsorption to an oppositely charged surface depends strongly on the charge density and corresponding swelling of the brush,²⁹ the charge and swelling effects of SDS binding should strongly alter SiO₂-*g*-PDMAEMA adsorption to silica. With the objective of achieving a more densely-packed layer of strongly charged BGNPs, we used a combination of three adsorption protocols to probe the role that SDS plays in the formation of BGNP layers: 1, adsorption from surfactant/BGNP mixtures to determine whether SDS enhances or inhibits adsorption at different levels of binding; 2, adsorption of surfactant to pre-adsorbed BGNPs, to determine if surfactants can bind to BGNPs and alter their physical characteristics while remaining adsorbed on the surface or whether they will simply drive BGNP desorption; and 3, cycled adsorption of surfactants and BGNPs, to determine whether it is possible to process a BGNP

adsorbed layer to achieve greater amounts of BGNP deposition by controlled exposures of an adsorbed layer to surfactant.

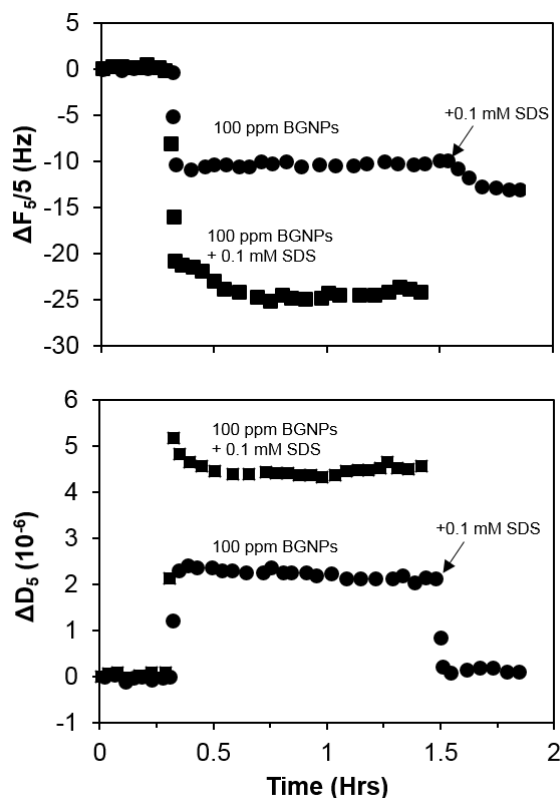


Figure 6.4. Sequential adsorption (circles) and co-adsorption (squares) of SiO₂-*g*-PDMAEMA with 0.1 mM SDS in 10 mM NaCl, pH 5. SDS was added at 1.4 h in the sequential adsorption experiment. Frequency (blue) and dissipation shifts (red) are shown for the 5th overtone and indicate that SDS binding to SiO₂-*g*-PDMAEMA alters the layer structure differently for co-adsorption or sequential adsorption.

BGNP/surfactant co-adsorption and sequential adsorption QCM-D

experiments are compared in **Figure 6.4** The QCM-D cells were initially filled with 10 mM NaCl at pH 5 and then subjected to either the pure, 100 ppm BGNP suspension or a mixture of 100 ppm BGNPs and 0.1 mM SDS, both at pH 5 in 10 mM NaCl. For sequential adsorption, the BGNP suspension was rinsed and

replaced with a 0.1 mM SDS solution after 1.5 h. In the first adsorption steps, both the pure BGNPs and the BGNP/SDS complexes adsorbed readily on the negatively charged silica surface, as expected at pH 5 due to the strong positive charge on the BGNPs that persists upon addition of low surfactant concentrations. The frequency and dissipation shifts are larger for adsorption of the BNGP/SDS complexes than for the pure SiO₂-*g*-PDMAEMA BGNPs. Two factors may contribute to the difference: the additional mass per particle contributed by the bound SDS and the possibility that a larger number of particles were adsorbed from the BGNP/SDS mixture due to the smaller particle size caused by brush collapse prior to adsorption. For sequential adsorption, binding of SDS to the pre-adsorbed SiO₂-*g*-PDMAEMA layer is indicated by a small decrease in frequency (small increase in adsorbed mass) and also a sharp drop in dissipation to within experimental error of zero. Since SDS increased the total adsorbed mass, the decreased dissipation cannot be attributed to BGNP desorption. The large decrease in dissipation upon SDS binding is attributed to brush collapse and the corresponding formation of a more rigid layer, consistent with the brush collapse observed in bulk suspension. It is important to note the differences between the final states of the co-adsorption and sequential adsorption curves in **Figure 6.4** which clearly indicate path-dependence, or hysteretic, effects in SDS/ SiO₂-*g*-PDMAEMA adsorbed layers as are typically observed when surfactants co-adsorb with linear polymers.

Next, we deposit BGNPs at either pH 5 or pH 9 then sequentially increase the SDS concentration, without intervening BGNP exposures or rinses. Independent ellipsometry

measurements in **Figure 6.5** provide direct indication of whether or not material is adsorbing or desorbing from the layer, complimentary to the QCM-D results in **Figure 6.6**. Ellipsometry shows that SDS binding continues to occur for each increasing concentration of SDS from 0.1 to 8.0 mM. For pH 5, the largest SDS addition occurs at 0.1 mM where the layer collapse is observed in QCM-D. After this collapse, SDS continues to adsorb but appears to approach saturation by the 8 mM level. At pH 9, the SDS addition occurs in a similar fashion, with high-affinity binding at 0.1 mM followed by an approach to saturation. The comparative binding for each SDS step is also shown in **Figure 6.5** where the surface excess concentration of bound SDS is plotted against concentration. Taking note of the initial adsorbed amounts, 2.5 and 0.8 mg/m² for pH 9.0 and pH 5.0 respectively, normalization of the data shows that SDS binds to similar extents under both pH conditions and thus suggests a similar mode of binding despite the vastly different charge states and brush conformations. Cooperative adsorption dominated by attraction among SDS tails is most likely occurring at the high SDS concentrations, as was observed by neutron reflectivity for planar PDMAEMA brushes and SDS³⁰. It is also important to note the desorption that occurs upon rinsing both layers, where it is clear that much of the bound SDS and possibly some of the SDS/BGNP complexes desorb during rinsing. This desorption at higher SDS concentration is contrary to experiments at low SDS concentrations (**Figure 6.7**) where no desorption was observed.

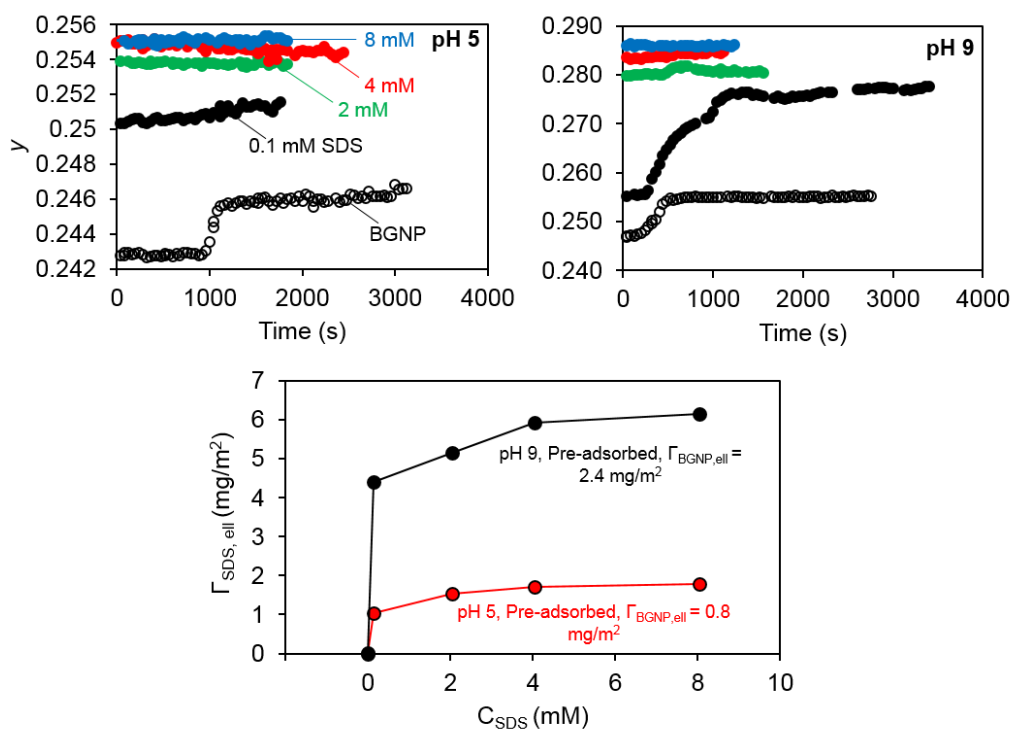


Figure 6.5. Sequential adsorption of SiO₂-g-PDMAEMA followed by increasing concentrations of SDS monitored by *in-situ* ellipsometry at pH 5 (top left) or pH 9 (top right). Binding isotherms (bottom) show the strong affinity of SDS under both strong and weak electrostatic attractions, indicating hydrophobic forces possibly dominating binding.

Figure 6.6 shows experiments where pre-adsorbed SiO₂-g-PDMAEMA BGNPs are sequentially exposed to particle-free 0.1, 2, 4, and 8 mM SDS solutions and the adsorption measured by QCM-D. The initial 0.1 mM step shows the behavior outlined earlier for both cases: at pH 5, the brush collapses (dissipation drops sharply to zero), while at pH 9 the layer maintains a softer, extended conformation as indicated by a nearly constant dissipation after SDS addition. For pH 5, SDS continues to adsorb to the layer for each increase in the surfactant concentration to 2, 4, and 8 mM. For pH 9 the layer undergoes a transient re-arrangement upon addition of 2 mM SDS, as the dissipation initially increases significantly then decreases to a level less than that before SDS addition. Subsequent increases in the surfactant concentration after this rearrangement at

2 mM produced results as were exhibited with the higher SDS concentrations at pH 5. This indicates that at high surfactant concentrations the mechanism for SDS incorporation into the layer does not depend strongly on pH. SDS is still being incorporated into the layer despite the large scale brush collapse and rigidification of the adsorbed layer, possibly suggesting cooperative binding dominated by hydrophobic or surfactant tail/polymer backbone interactions at higher surfactant concentrations.

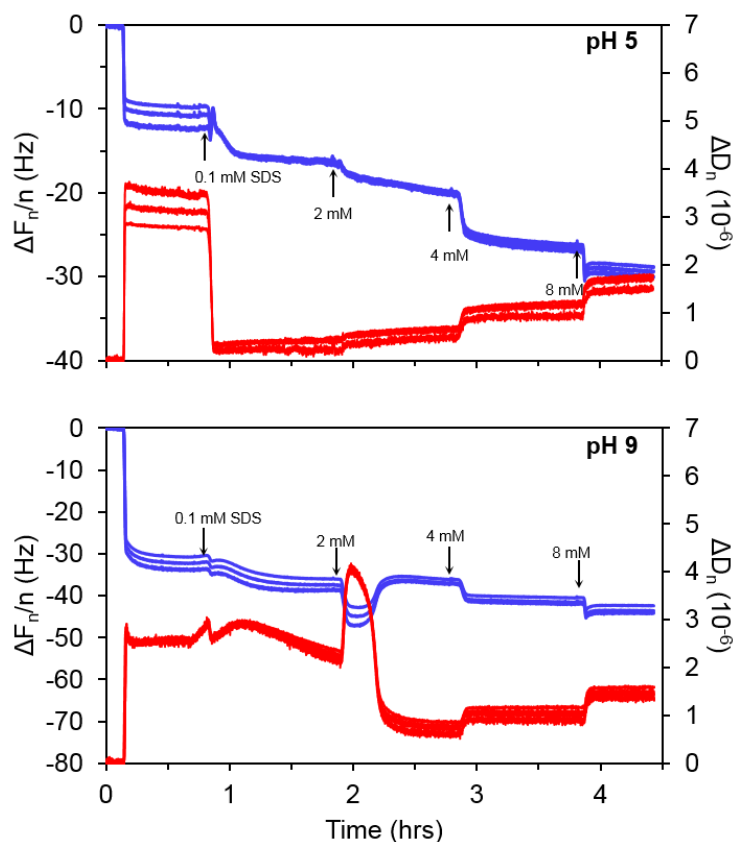


Figure 6.6. Sequential adsorption of SiO₂-g-PDMAEMA followed by increasing concentrations of SDS monitored by QCM-D at pH 5 (top) or pH 9 (bottom). The first step is BGNP adsorption and rinsing. Arrows identify the injection point for SDS at the given concentration.

6.3.3 Cycled nanoparticle/surfactant adsorption for enhanced particle packing.

The QCM-D results in **Figure 6.3** showed that SiO₂-g-PDMAEMA layers respond to low concentrations of added SDS by forming a rigid, collapsed brush similar

to bulk behavior. This collapse and subsequent rinsing indicated that the surfactant is strongly incorporated into the brushes of the adsorbed BGNPs. The observation that transient SDS exposure can produce a persistent change in the state of the brush on each adsorbed SiO₂-*g*-PDMAEMA BGNP suggests that it might be possible to manipulate the extent of adsorption and the resulting layer mechanical properties by multi-step sequential cycling of exposure to BGNPs, surfactants and rinsing solutions. Thus, we exposed the surface to repeated doses of SiO₂-*g*-PDMAEMA and SDS and monitored whether adsorption continued in each stage by QCM-D. **Figure 6.7** shows the results of cycled adsorption experiments in 10 mM NaCl at pH 5 and pH 9, where the bulk was cycled between 100 ppm SiO₂-*g*-PDMAEMA suspensions and SDS solutions that were increased step-wise in concentration from 0.1-0.5 mM SDS with each subsequent exposure. The cell was rinsed with 10 mM NaCl after each step, so that the bulk would only contain the BGNPs or surfactants, but not both.

At pH 5, the frequency decreased every time that SiO₂-*g*-PDMAEMA or SDS was added, indicating a monotonic increase in adsorbed mass throughout the cycling process. The spread in overtones during each BGNP adsorption step suggests the layer is viscoelastic, consistent with the large dissipation values. This is likely due to the swollen state of the PDMAEMA brushes on the newly adsorbing SiO₂-*g*-PDMAEMA BGNPs as they join a layer that had consisted of BGNPs with irreversibly collapsed, SDS-treated brushes. The layers must be heterogeneous with some composition of pure BGNPs and BGNP/SDS complexes at each of the SiO₂-*g*-PDMAEMA adsorption stages. The dissipation signal rapidly dropped to nearly zero, and the different overtones collapsed onto each other for both frequency and dissipation, every time SDS was added. This indicates that SDS binding induced brush collapse in the adsorbed SiO₂-*g*-PDMAEMA BGNPs and rigidified the adsorbed layer, further highlighting the fast dynamics

associated with SDS uptake and its influence on brush conformation. Each time that fresh, SDS-free SiO₂-*g*-PDMAEMA BGNPs were added, the dissipation increased and the frequency decreased again, and the spread in the overtone curves became more pronounced with each subsequent addition. This “re-swelling” of the layers is attributed to the adsorption of the new BGNPs with their highly swollen brushes. This behavior is consistent with monotonic increases in the number of adsorbed BGNPs, as evidenced by the continuous drop in frequency, whereas the dissipation shift seems to track the average brush conformation of the adsorbed BGNPs.

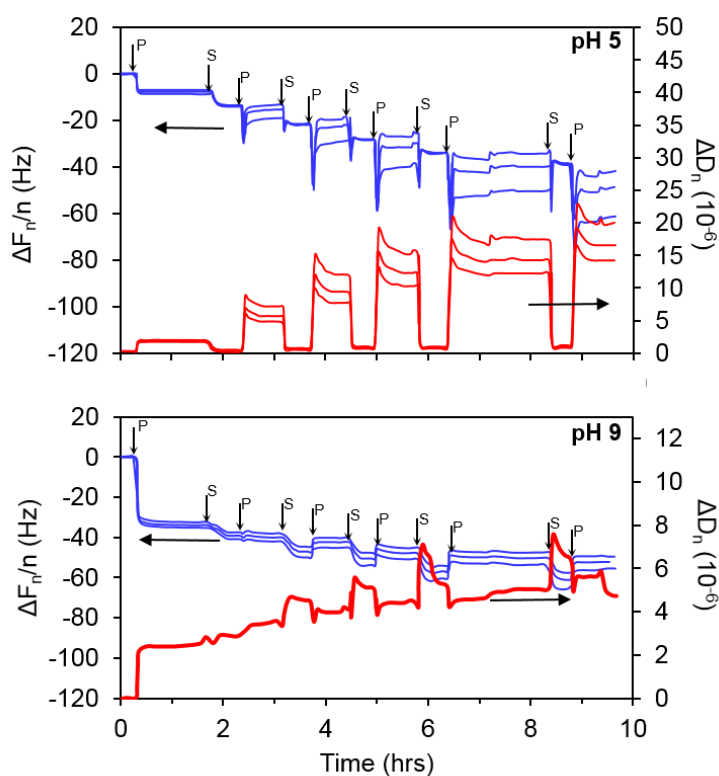


Figure 6.7. Cycled adsorption of SiO₂-*g*-PDMAEMA BGNPs (labeled P) and SDS (labeled S) at pH 5 (top) and pH 9 (bottom). SDS concentration increased for each injection as follows: 0.1, 0.2, 0.3, 0.4, 0.5 mM. The cell was rinsed with 10 mM NaCl solution after each BGNP or SDS step with no change in either signal. Frequency shifts (blue) and dissipation shifts (red) are shown for the 5th, 7th, and 9th overtones. All overtones overlap for pH 9 dissipation traces. Note the difference in scale between the top and bottom dissipation axes.

Similar increases in deposition are observed at pH 9, with continuous frequency decrease throughout the surfactant/BGNP cycles suggesting continued addition of material through each sequential adsorption stage. The primary difference between pH 9 and pH 5 lies in the response of the dissipation signal. At pH 9, the dissipation increases upon surfactant addition and drops upon addition of BGNPs -- the reverse of what was observed at pH 5. Recall, at pH 9 the brush is already collapsed and surfactant likely binds along the periphery of the brush. Thus, addition of surfactant to the adsorbed particles generates a softer layer at pH 9. This is likely caused by the reversal of net charge on the adsorbed particles, allowing for additional, weakly positively charged and slightly more swollen SiO₂-*g*-PDMAEMA BGNPs from the bulk suspension to enter the adsorbed layer. Packing of BGNPs can be increased by either decreasing the charge on the particles or screening the length scale of the electrostatic interactions. Here, addition of SDS decreases the charge enabling fresh positively charged BGNPs to access the surface and attach.

Representative AFM images for single-step SiO₂-*g*-PDMAEMA adsorbed layer and a SiO₂-*g*-PDMAEMA/SDS cycled layer are provided in **Figure 6.8**, and greatly enhanced particle deposition is observed after alternating 100 ppm SiO₂-*g*-PDMAEMA and 0.1 mM SDS adsorption for 4 full cycles, again owing to the uptake of surfactant and the effect that it has on the lateral forces between SiO₂-*g*-PDMAEMA particles at the interface. For single step adsorption there are ~17 BGNP/μm² and ~125 BGNP+SDS complexes/μm² after cycled adsorption.

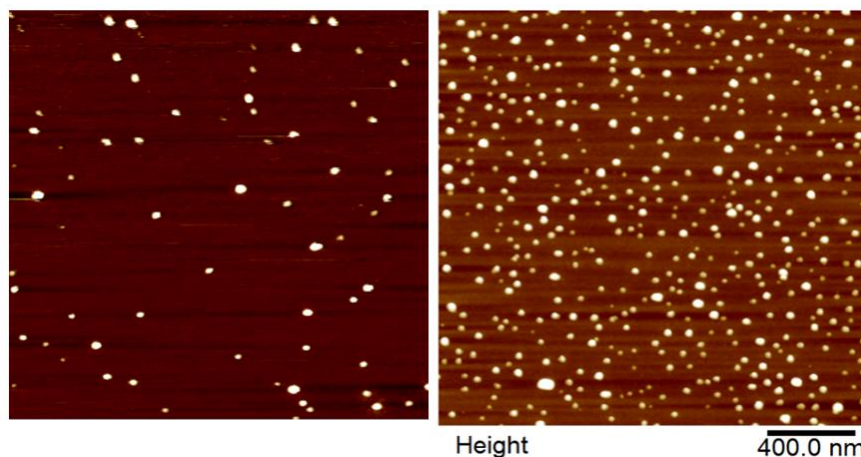


Figure 6.8. AFM images of dry SiO₂-g-PDMAEMA adsorbed layers on silica. *Left:* SiO₂-g-PDMAEMA adsorption at pH 5 for 1 hour. *Right:* Surfactant-processed adsorbed layer, after 3 cycles of alternating SiO₂-g-PDMAEMA → SDS adsorption, rinsing in between.

6.3.4 Influence of bound surfactant on surface forces

The results above establish that surfactant binding strongly effects BGNP layer formation and conformation. This must have implications for surface forces between BGNP coated surfaces, which are important for designing colloidal stabilizers or lubricants. **Figure 6.9** shows the effect of SDS binding on the normal compressive forces between two silica surfaces, a flat oxidized wafer and a silica sphere, both displaying adsorbed SiO₂-g-PDMAEMA with a background electrolyte of 10 mM NaCl at pH 5. The BGNP coated surfaces with no added surfactant display electrosteric repulsions upon approach (the force decay length of 25 nm far exceeds the 3 nm Debye length for 10 mM NaCl, indicating that the long-range force is not the electrostatic double layer force) and display strong adhesion upon retraction of the two surfaces.

Upon addition of 0.1 mM SDS, the range of the repulsions decreases due to SDS binding and collapsing the brush, with the force decay length decreasing to approximately 5 nm. This surfactant-induced brush collapse is consistent with QCM-D and ellipsometry measurements shown in **Figure 6.3**. The effective reduction of repulsive forces is also apparent from the shift in distance where the forces begin to sharply rise on a log-lin plot of force vs. separation. SDS binding is also evidenced by a strong reduction in the adhesive force upon retraction, owing to a reduced number of bridging contacts that form when the surfaces are brought into contact. The particle brushes remain collapsed upon increasing the SDS concentration to 1.0 mM SDS, consistent with the low dissipation signal in observed via QCM-D. Little change was observed in the repulsive force upon approach of the surfaces, but the adhesion force was further reduced with 1.0 mM SDS, consistent with more bound surfactant and fewer positively charged polymer segments available to bridge the opposing surfaces.

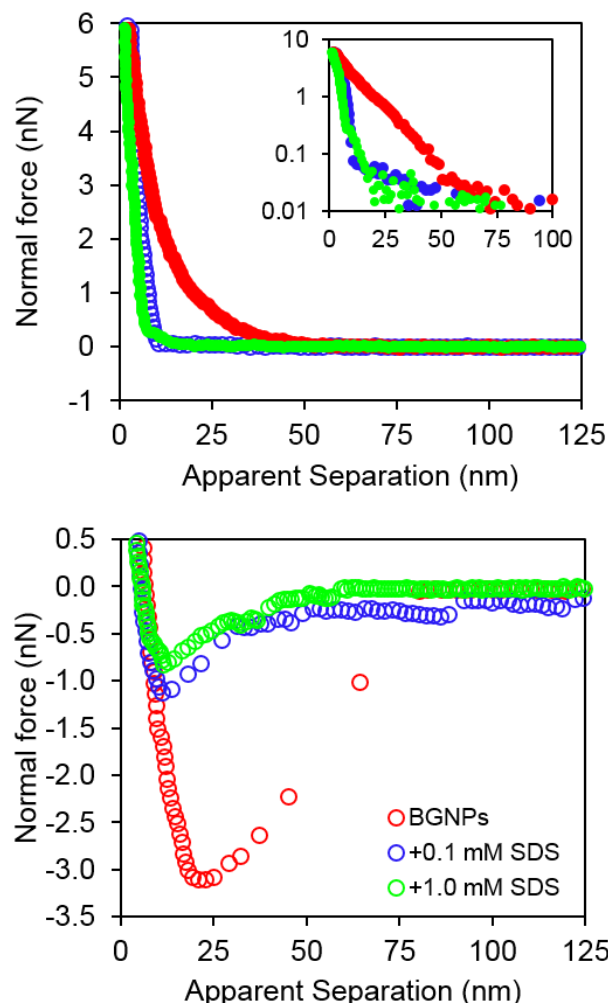


Figure 6.9. Colloidal probe AFM force profiles between a 20 micron diameter silica sphere and a flat silica surface, both with adsorbed SiO_2 -*g*-PDMAEMA, in 10 mM NaCl at pH 5. Sphere has a lower coverage of particles than the surface, intentionally to induce strong bridging. Red points are the particle decorated surfaces in NaCl solution and blue/green are the same surfaces after addition of SDS. *Top*: force curves on approach, with inset on log-lin scale. *Bottom*: force curves on retract, zoomed in on the adhesive regions.

These results show that while SDS complexation reduces the range of repulsive forces that resist contact between opposing SiO_2 -*g*-PDMAEMA-decorated surfaces it also decreases the adhesion force once those surface do come into contact. These effects may be mutually antagonistic in the sense of

surface engineering layers in friction applications where lubricity and surface protection are desired.

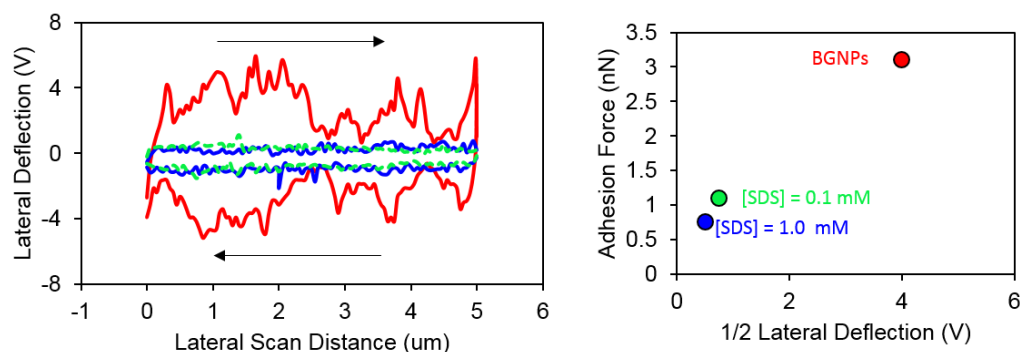


Figure 6.10. Friction properties of silica surfaces coated with SiO₂-g-PDMAEMA with and without bound SDS. *Left:* Colloidal probe lateral force measurements between a 20 μm silica sphere and flat silica surface, each coated with BGNPs in the absence SDS (red) and in the presence of 0.1 mM SDS (green) or 1.0 mM SDS (blue). Arrows indicate the sliding direction of the probe. Applied load is 4.0 nN and sliding speed is 5.0 μm/s. *Right:* Correlation between the strength of the normal adhesive force and the average lateral friction force as indicated by the lateral cantilever deflection.

The adhesive force between surfaces has a strong effect on frictional forces between surfaces undergoing sliding motion under an applied load, as shown in **Figure 9**. Frictional forces were compared for adsorbed SiO₂-g-PDMAEMA layers with and without SDS. Using colloidal probe lateral force microscopy the SiO₂-g-PDMAEMA-decorated surfaces were first brought into contact under an applied load of 4 nN and then sheared at 5 μm/s to measure frictional forces. The friction force without SDS was high compared to forces measured in the presence of SDS. Strong bridging also appears to result in stick-slip motion as the inter-surface bridging contacts form and break dynamically. Adding 0.1 or 1.0 mM

SDS strongly reduced the friction forces and smoothened the sliding motion under the same 4 nN load. At constant load, it is fair to assume that the friction measurements are performed with the same number of BGNP or BGNP/SDS complexes in the contact area during sliding. The reduction in friction caused by SDS can be directly correlated with the reduced strength of the adhesion between surfaces in contact. Thus, the net effect of the concurrent reduction in the range of the normal electrosteric repulsion force and in the magnitude of the bridging adhesion forces was to produce an overall decrease in friction between SiO₂-*g*-PDMAEMA-decorated surfaces and the elimination of stick-slip motion. Similar effects have been observed in SDS bound to physisorbed bottle-brush polymer layers²¹. This is potentially useful as surfactant could provide a means for rapid, external, non-destructive switching of friction and adhesion in BGNP-based lubrication schemes.

6.4 Conclusions

SDS forms complexes with cationic PDMAEMA brush-grafted nanoparticles under both strongly charged (acidic) and weakly charged (basic) solution conditions. At pH 5, surfactant binding results in brush collapse, the degree of which increases with increasing SDS concentration. SDS monomers penetrate the extended, curved brush and bind to the protonated amine groups, weakening the segment-segment electrostatic repulsions and thereby collapsing the brush. Conversely, at pH 9 the brush is initially de-swollen and SDS is left to bind to residually charged groups on the brush exterior, resulting in a net charge reversal of the complex under the same dilute SDS conditions. Two regimes of surfactant binding are identified: 1) at low concentrations, SDS is strongly incorporated into the brush and persists in the layer upon various rinse cycles,

and 2) at higher concentrations, SDS cooperatively forms loosely-bound complexes that are reversibly adsorbed and can be rinsed. This work identifies distinct dynamic and conformational differences attributed to swelling and de-swelling of the brush upon changes in solution pH and the more drastic brush collapse upon uptake of SDS. SDS-binding is leveraged to process brush-grafted nanoparticle layers and provide a route for enhanced particle deposition that is unachievable by pH or ionic strength processing schemes. The extent of SDS binding also plays a vital role in determining the strength of interactions between surfaces decorated with adsorbed SiO₂-*g*-PDMAEMA/SDS complexes, providing a route to control adhesive bridging and frictional forces without changing solution pH or ionic strength conditions. Formation of weak polyelectrolyte BGNP/surfactant complexes in the bulk and at surfaces might potentially be used to generate smart films, where brush conformational changes can be induced by external stimuli such as pH, to varying degrees of responsiveness based on the amount of complexed surfactant they contain.

6.5 References

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7. Integration of star polymers and polymer brush nanoparticles into multilayer films

This chapter includes methods for building multi-layer films with polymer brush nanoparticles using layer-by-layer sequential adsorption with various polymeric counterparts. Layer-by-layer (LbL) assembly has developed over the past decades as a simple and robust method for forming novel films and surface coatings¹⁻³. LbL assemblies are most commonly built by the sequential adsorption of oppositely charged polyelectrolytes, colloids, or nanoparticles. Other systems based on hydrogen-bonding polymers and nanoparticles have also been successfully employed in LbL schemes⁴, expanding the inventory of LbL building blocks to include a number of common, non-ionic polymers. Given the large selection of starting materials (chemistry, structure, and physical properties), processing routes (*i.e.* spin-assisted vs dip-assisted adsorption) and processing conditions (solvent, pH, and ionic strength), LbL films offer unique pathways for generating films with tailored composition and properties. For example, all-star polymer multilayer films have shown interesting morphological behavior relative to linear polymer multilayers⁵, with drastic layer changes with respect to pH alterations. Additionally, polymeric multilayer films have shown improved wear resistance properties due to increased layer thickness and mechanical properties^{6,7}. Therefore, one may expect lubricating layers of polymer brush nanoparticles can benefit from increased thicknesses afforded by layer-by-layer schemes. This chapter is separated into two sections that deal with mixed polymeric and multilayer films.

7.1 Mixed adsorbed layers of polyelectrolyte brush-grafted nanoparticles with non-ionic star polymers

This section investigates how the adhesive bridging forces arising in sub-monolayer cationic brush-grafted nanoparticle (SiO_2 -*g*-PDMAEMA, or BGNP PDMAEMA) adsorbed layers, discussed in **Chapter 5** can be suppressed by “backfilling” these heterogeneous adsorbed layers with non-ionic poly(ethylene oxide) star copolymer (star PEO). Sequential adsorption of BGNP PDMAEMA and star PEO successfully generates high-coverage mixed nanoparticulate brush layers with uniformly repulsive normal forces and smoother, reduced friction forces than pure BGNP PDMAEMA layers. Adsorption and force measurements reveal that star PEO adsorbs to silica but also binds to BGNP PDMAEMA, and sequential adsorption of the two components forms mixed multi-layers. Colloidal probe force measurements show that BGNP PDMAEMA/star PEO multilayers maintain smooth frictional sliding under strong loads, demonstrating their potential usefulness as aqueous boundary lubricants.

7.1.1 *Backfilling electrostatically patchy layers with non-ionic star polymers*

In an effort to prevent bridging adhesion caused by exposed underlying silica surface, we will investigate the sequential adsorption of star PEO to a pre-adsorbed SiO_2 -*g*-PDMAEMA layer. Ideally, star PEO will pack densely in the space between adsorbed SiO_2 -*g*-PDMAEMA particles and generate a high surface coverage, mixed cationic/non-ionic brush nanoparticle adsorbed layer. We have shown in **Chapter 3** that star PEO adsorbs in a dense, brush-like surface on silica with an apparent coverage of 60-70%, therefore making it a logical choice as a non-ionic coating for the exposed surface. Similar strategies have been used by

the Santore research group to generate electrostatically patchy layers through the sequential adsorption of cationic polymers, proteins, and nanoparticles followed by “backfilling” with a bottle-brush PEO polymer^{8–10}. These studies aim to generate surfaces that can capture and adhere particles and colloids. No attempts have been made to assess the direct frictional forces for employing these mixed layers as lubricants.

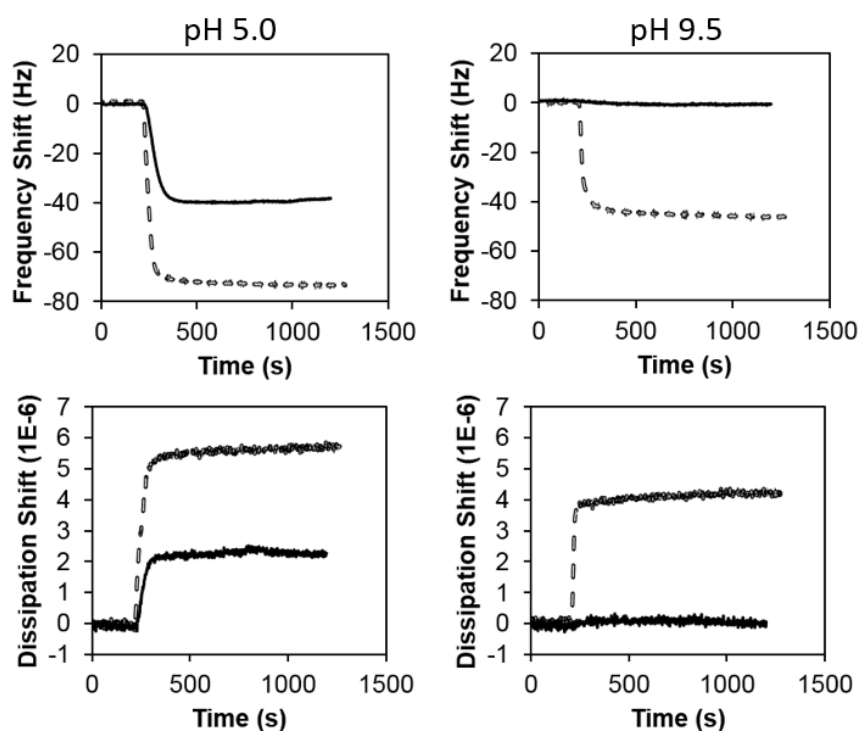


Figure 7.1. Adsorption of star PEO from a 100 ppm suspension in 1 mM NaCl on bare silica (solid lines) and on silica pre-coated with BGNP PDMAEMA (dashed lines) measured at pH 5.0 (left column) and pH 9.5 (right column) by QCM-D. The initial adsorbed amount of BGNP PDMAEMA is less at pH 5.0 than at pH 9.5, but both have been baselined to zero at initial times here.

Recalling the adsorption behavior of BGNP PDMAEMA from **Chapter 4**, there exists a narrow pH window where dense packing is achievable on the surface. The adsorption maximum occurs at a pH near the isoelectric point of the

charged particles. Outside of this narrow window, the particles will deposit sparsely on the surface and result in bridging adhesion during interaction with an opposing, sparsely coated surface. Therefore, it is desirable to block the particle-surface bridging attraction by coating the remaining substrate with a non-ionic polymer when the deposition pH is outside of the range pH 9.0 – 9.3.

Figure 7.1 shows QCM-D measurements for adsorption of star PEO to bare silica and BGNP PDMAEMA coated silica surfaces. This allows for the comparison between direct adsorption and “backfilling” via sequential adsorption. At pH 5.0, BGNP PDMAEMA adsorbs to a low extent due to the strong lateral repulsions between highly charged particles. star PEO adsorption to silica at pH 5.0 is also shown in **Figure 7.1**, where star PEO reaches frequency and dissipation shifts of approximately -40 Hz and 2×10^{-6} , respectively on the bare substrate. In the presence of a BGNP PDMAEMA pre-coated layer, additional frequency and dissipation shifts (beyond those produced by BGNP PDMAEMA pre-adsorption) reach approximately -70 Hz and 5.5×10^{-6} . This result suggests that Star PEO adsorbs to a larger extent on the pre-coated surface than the bare surface. The same experiments are performed at pH 9.5, where BGNP PDMAEMA again adsorbs sparsely due to reduced particle-surface attractions. However, unlike at pH 5.0, star PEO does not adsorb on bare silica at pH 9.5. This is evidenced by the zero shift in frequency and dissipation shown in **Figure 7.1**. Nevertheless, when the silica surface is pre-coated with BGNP PDMAEMA, star PEO adsorption is observed, and shifts of -48 Hz and 4.0×10^{-6} are reached under normally non-adsorbing pH conditions. Both sequential adsorption results

at pH 5.0 and 9.5 indicate binding of star PEO to the pre-adsorbed BGNP PDMAEMA. This had been unexpected. It is possibly explained by hydrogen bonding interactions or arm-core interactions between the two branched nanoparticulate brush materials. Interactions between the star PEO and BGNP PDMAEMA is further evidenced in measurements of the electrophoretic mobility distribution for a mixture of star PEO and BGNP PDMAEMA. The mixture exhibits a mobility that is intermediate to the neutral star PEO and the cationic BGNP PDMAEMA.

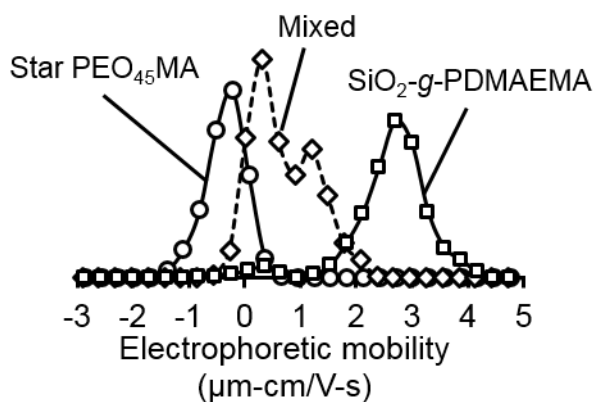


Figure 7.2. Electrophoretic mobility distributions for 1.0 mg/mL brush nanoparticle dispersions in 1 mM NaCl. Mixture is equal parts BGNP PDMAEMA and star PEO.

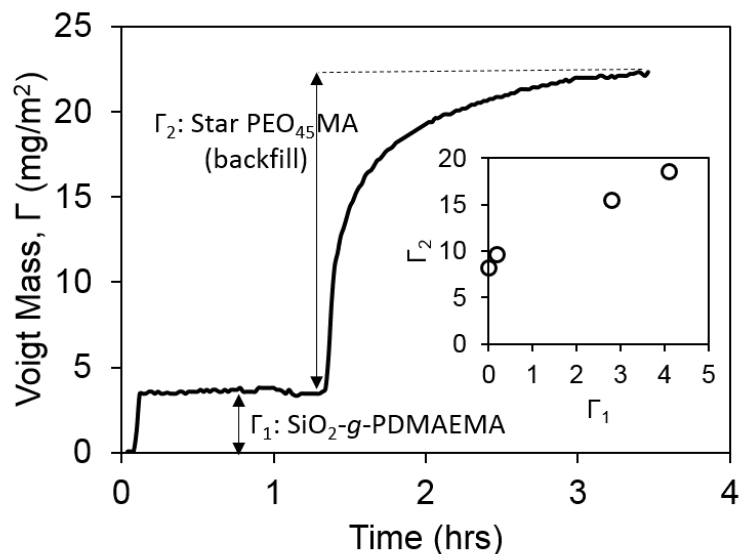


Figure 7.3. Adsorbed mass during star PEO backfill of BGNP PDMAEMA on silica, measured by QCM-D. Data is evaluated using the Voigt model. *Inset:* Variation of the mass added during backfill Γ_2 as a function of the pre-adsorbed BGNP amount Γ_1 . The increase in Γ_2 as a function of Γ_1 , or decreasing exposed silica surface area, indicates binding of star PEO to the pre-adsorbed BGNPs.

Figure 7.3 again shows QCM-D sequential adsorption measurements, however now represented by the modeled Voigt adsorbed mass instead of raw frequency and dissipation shifts. Here, SiO₂-g-PDMAEMA is first adsorbed in the charged state resulting in a relatively low coverage adsorbed layer given by the first surface excess concentration plateau, Γ_1 . After rinsing SiO₂-g-PDMAEMA from the bulk, star PEO is introduced and adsorption readily occurs. The large increase in the adsorbed mass as sensed by QCM-D indicates successful incorporation of star PEO into a mixed layer, and the additional mass during backfilling is represented by the approach to a second plateau, Γ_2 , which had not quite been achieved. The adsorption measurement here has been conducted at a lower flow rate than those in **Figure 7.1**, explaining the slower backfilling

adsorption kinetics. The inset in **Figure 7.3** shows the relationship between the pre-adsorbed BGNP amount Γ_1 and the backfilled amount Γ_2 . The increasing trend again suggests that star PEO must be adsorbing to the BGNP PDMAEMA particles. Available bare surface area decreases as Γ_1 increases, and if star PEO adsorption only occurred on the surface, Γ_2 would decrease as a function of Γ_1 . While the exposed silica surface area decreases, the total surface area increases with Γ_1 due to roughness imparted by the adsorbed particles, and if there exists some binding affinity between star PEO and BGNP PDMAEMA then one would expect Γ_2 to increase as a function of Γ_1 .

The presence of a mixed layer is verified by AFM imaging before and after backfilling, shown in **Figure 7.4**. The smooth bare surface is clearly identifiable in the region between isolated, adsorbed SiO₂-g-PDMAEMA particles prior to backfilling, and a dense monolayer of star PEO forms in between SiO₂-g-PDMAEMA particles after backfilling is performed. Representative height profiles across three adsorbed SiO₂-g-PDMAEMA particles shows the presence of star polymer after backfilling in the previously smooth bare silica surface regions. Image analysis of the star PEO regions indicate an area coverage of ~75%, indicating a very close packed monolayer. SiO₂-g-PDMAEMA have an average adsorbed diameter $d_{BGNP} = 65.3 \pm 13$ nm and star PEO have an average adsorbed diameter of 18.8 ± 3 nm. The relative sizes of the collapsed particles in air are consistent with those made by DLS measurements of the stars and particles swollen in aqueous suspension.

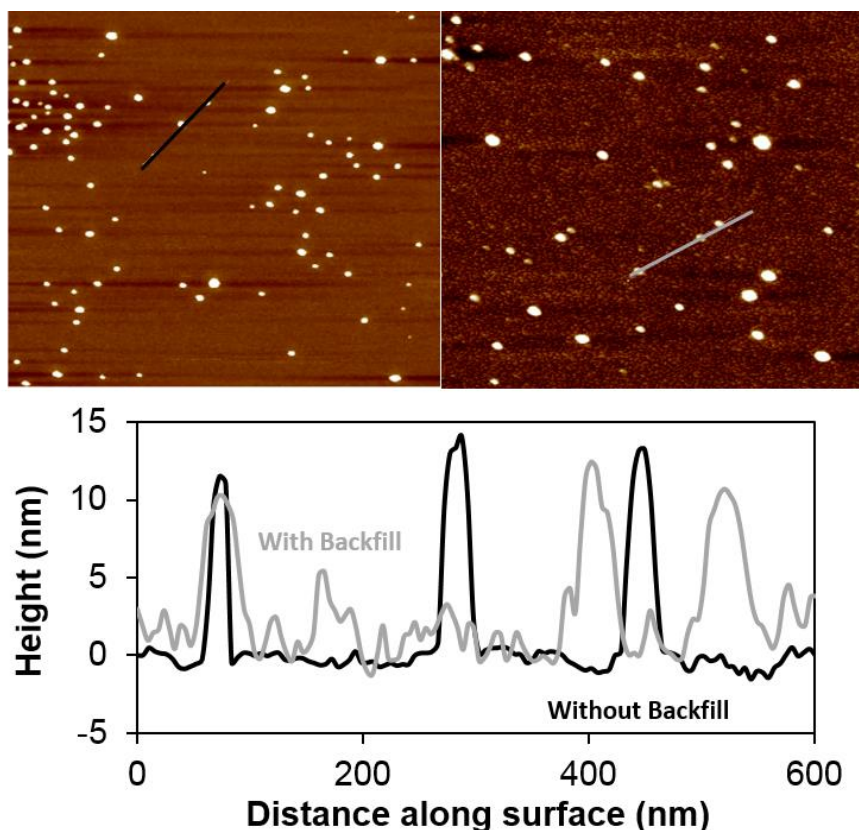


Figure 7.4. Star PEO backfill of BGNP PDMAEMA after drying the layer and imaging by AFM in air. *Top left:* Only BGNP PDMAEMA adsorbed on silica. *Top right:* Backfilled with star PEO at pH 5.0. *Bottom:* Height profiles traversing three adsorbed BGNPs. Without backfill, the smooth silica surface is visible between particles. With backfill, the interparticle space is rough from the presence of a dense star PEO layer now on the surface.

The implications of star PEO backfilling on the normal and frictional forces is shown in **Figure 7.5**. Normal force profiles between BGNP PDMAEMA coated silica surfaces again show the weak repulsions on approach and adhesion on retraction associated with the low coverage adsorbed layer. Star PEO is then introduced, allowed to adsorb, and rinsed from the cell. Force curves after backfilling display much longer range repulsions, and no adhesive forces are measured upon retraction of the surfaces. This result is consistent with the

formation of a high-coverage adsorbed layer after backfilling, effectively masking the underlying substrate and preventing inter-surface bridging. The longer range repulsions are also consistent with the picture that star PEO binds to adsorbed BGNP PDMAEMA, effectively increasing the apparent steric thickness of the layers. Lateral forces are measured on the same adsorbed layers and a 5-fold reduction of friction is observed after backfilling for an applied normal load of 5.4 nN and a sliding speed of 1 $\mu\text{m/s}$. The results in **Figure 7.5** indicate that simple sequential adsorption is a viable route for preventing bridging forces and reducing friction between adhesive, low-coverage particle layers.

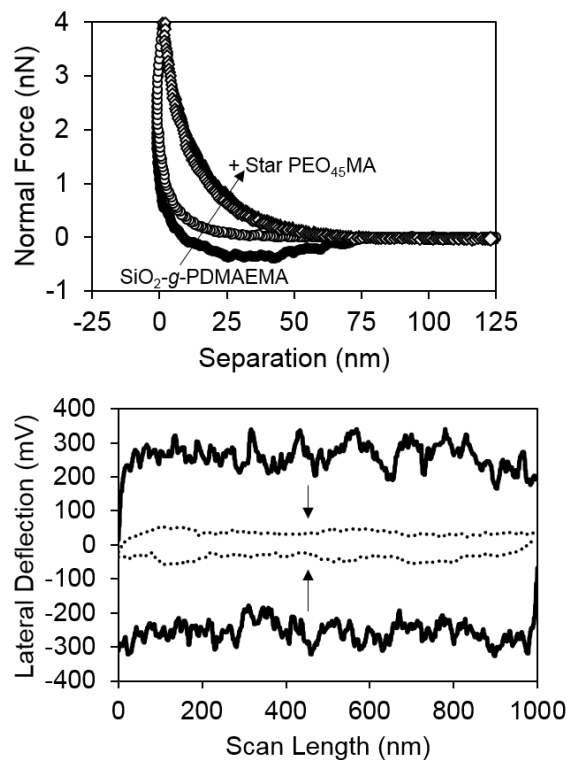


Figure 7.5. *Top:* Colloidal probe normal force profiles between a 10 μm radius silica sphere and flat silica surface first coated with BGNP PDMAEMA (circles) then backfilled via addition of star PEO (diamonds). In 1 mM NaCl, pH 5.0. *Bottom:* Colloidal probe lateral force loops obtained at an applied load $F_n = 5.4$ nN and a sliding speed of 1 $\mu\text{m/s}$ for BGNP PDMAEMA (solid line) and after backfilling the same BGNP layer with star PEO (dotted line). Note that the lateral

deflection signal in mV is proportional to the friction force between layers, and the same probe and cantilever are used for each measurement.

7.1.2 *Multi-layer adsorption of BGNP PDMAEMA and star PEO*

The observation that star PEO binds to BGNP PDMAEMA on the surface enables further sequential adsorption and the formation of multilayer films via the “layer-by-layer” deposition strategy. **Figure 7.6** shows the successful formation of multilayer films consisting of star PEO and BGNP PDMAEMA. First, multilayer formation is observed by QCM-D/ellipsometry. Here, each BGNP PDMAEMA adsorption step shows a small increase in thickness, followed by a more prominent star PEO binding step. Done sequentially, thicker layers are formed as indicated by the monotonically increasing Voigt adsorbed mass. A total of three binary layers are assembled in this experiment, but much thicker multilayers are grown in the next section. Secondly, the multilayer growth is observed by colloidal probe force measurements. The normal force versus distance profiles in **Figure 7.6**, plotted in log-lin coordinates, show the onset of steric interactions between mixed multilayers on approach and retract. This steric overlap is indicative of the relative layer thicknesses, and we see that the interactions shift to longer ranges over the course of $n = 1, 2, 3$ multilayer formation. The force curves are all purely repulsive since the multilayers are capped with star PEO, masking the small amounts of incorporated BGNP PDMAEMA that allow multilayering to continue. The differences between compression and retraction of the layers indicates some rate-dependent energy dissipation due to changes in layers in layer conformation. The slopes during

indentation of the layers indicates different mechanical properties. It is clear from both the adsorption and force measurements that thicker layers can be assembled in this sequential adsorption method.

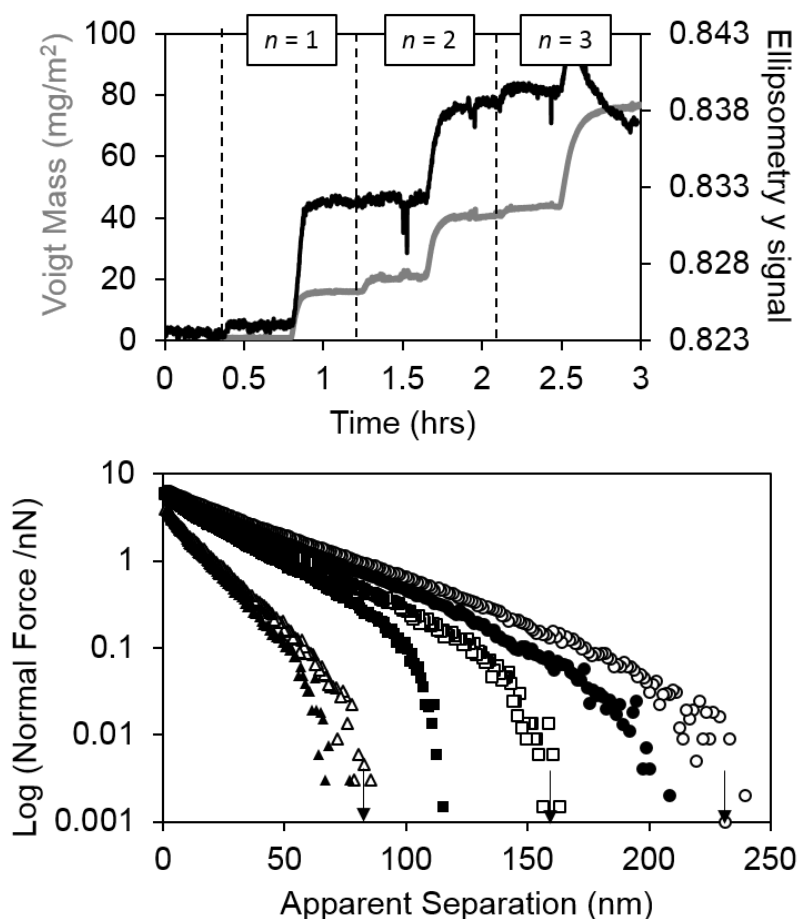


Figure 7.6. Multilayers formed by sequential adsorption in 1 mM NaCl, pH 5. *Top:* probed by simultaneous QCM-D (grey line) and ellipsometry (black line). Addition of BGNP PDMAEMA and star PEO result in a single mixed “binary” layer, designated n . *Bottom:* Force profiles on approach (filled) and retraction (open) between a 10 micron glass colloidal probe and a flat silica surface coated with mixed multilayers of BGNP PDMAEMA and star PEO. The sharp increase of repulsive forces is caused by the onset of steric repulsions, located at distances marked by the arrows that increase with number of layers deposited.

The friction versus load profiles of the mixed multilayer films are shown in **Figure 7.7**. Also included are the pure component BGNP PDMAEMA and Star PEO behaviors. For BGNPs that exhibit bridging adhesion, as depicted here, the coefficient of friction is greatly reduced upon backfilling with Star PEO. The backfilled layer, $n = 1$, displays a coefficient of friction that is ~ 6 times lower than the patchy BGNP layer and is only slightly higher than a pure star PEO layer. The coefficient of friction is approximately the same for $n = 3$ layers, but increased slightly for $n = 2$ multilayers. This is likely related to the energy dissipation displayed in the normal force profiles (manifest as hysteresis between forces measured on approach and retraction), indicating some rate-dependent layer relaxation that occurs during compression and influences the sliding behavior. All multilayers display relatively low coefficients of friction relative to the patchy surface, and demonstrate that backfilling can be successfully employed to control adhesion and friction in these mixed brush nanoparticle systems.

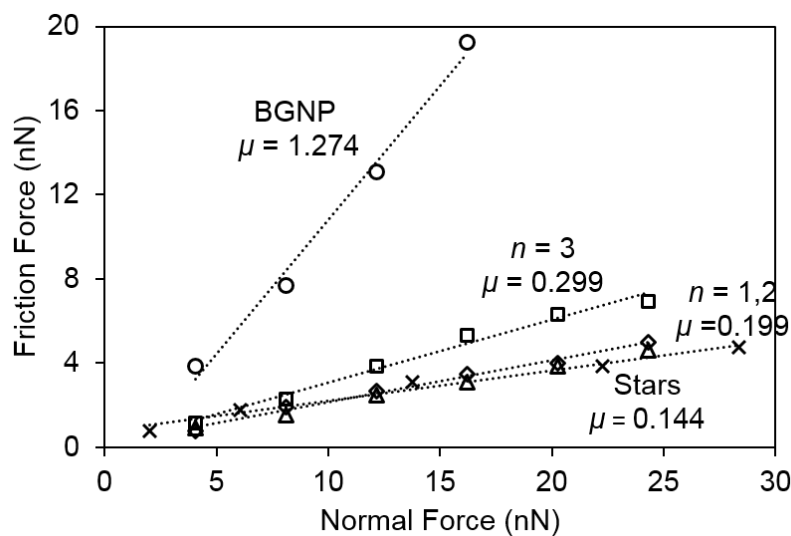


Figure 7.7. Friction versus load measurements between a 10 μm glass probe and a silica surface coated with SiO_2 -*g*-PDMAEMA (BGNPs, circles), star PEO

(crosses), and binary layers: $n = 1$ (backfilled, triangles), $n = 2$ (diamonds), $n = 3$ (squares). Coefficients of friction μ are calculated as the slope of the best fit lines (dotted). Note, the BGNPs displayed adhesive normal force vs. distance profiles, while the remaining layers displayed purely repulsive force curve profiles. All measurements are in 1 mM NaCl, pH 5 – 6.

7.2 Layer-by-layer assembly with linear polyanions

Here we present a study of the influence of polymer architecture on the buildup of layer-by-layer polymer films. We utilize three structurally distinct cationic polyelectrolytes based on poly(2-(dimethylamino ethyl) methacrylate) (PDMAEMA): linear PDMAEMA, 14-arm PDMAEMA star polymers (Star PDMAEMA), and PDMAEMA brush-grafted silica nanoparticles (BGNP PDMAEMA) and study thin film assembly of these polycations with linear poly(acrylic acid) (PAA), linear polystyrene sulfonate (PSS), and a non-ionic core-crosslinked poly(ethylene oxide) star polymer (Star PEO). Extent of adsorption is measured by *in-situ* quartz crystal microbalance with dissipation and complimented with ellipsometry and AFM imaging. The compressive and shear forces between multi-layer films are interrogated using colloidal probe atomic force microscopy to demonstrate the enhanced mechanical stability of the layers under strong compression and sliding.

7.2.1 Influence of polycation architecture on LbL multilayer formation

Table 7.1. Degree of polymerization and architecture of polymers used in LbL

Polymer Type	f , # of chains	N , DP	fN
<i>Spherical Polymers</i>			
BGNP PDMAEMA	175	140	24500
Star PDMAEMA	14	62	868
<i>Linear Polymers</i>			
PDMAEMA	1	575 (90k)	
PAA	1	278 (20k)	
PSS	1	380 (70k)	

Layer-by-layer adsorption of linear, star, and BGNP PDMAEMA with linear polyanions PSS and PAA was first assessed using QCM-D. The molecular characteristics of the polymers are specified roughly in **Table 7.1**. LbL of the different grafted polycations with linear polystyrene sulfonate (PSS, $M_w = 70,000$) is shown in **Figure 7.8**. PSS is a strong polyelectrolyte and bears a negative charge that is independent of pH, meaning that all the sulfonate groups will be negatively charged in aqueous solution. LbL is performed in 1 mM NaCl at pH 5 so that the PDMAEMA polymers are positively charged. Multilayering is clearly observable via QCM-D by the continuously decreasing frequency shifts and increasing dissipation shifts incurred on each adsorption step. A total of 8 polycation/polyanion adsorption cycles are completed. Additionally, architecture plays a role in the adsorbed mass during LbL. The frequency and dissipation shifts are largest for BGNP PDMAEMA, followed by the 14-arm Star PDMAEMA, and last the linear PDMAEMA. This is possibly due to the compact

nature of the BGNP and star polymers and their ability to bind more polyanion per polymeric unit, thus increasing the adsorbed mass per step. The mechanism is not clear via QCM-D, but the overall adsorbed mass does depend on architecture. LbL is also performed with linear poly(acrylic acid) (PAA, $M_w = 20,000$). In contrast to the strong polyelectrolyte PSS, PAA is a weak polyelectrolyte whose degree of ionization will depend on acid base equilibrium and pH. PAA obtains a negative charge by de-protonating carboxylic acid groups along the backbone. QCM-D measurements are again performed using PAA and the linear, star, and BGNP PDMAEMA for comparison with linear PSS. The QCM-D data shown in **Figure 7.9** for PAA exhibits different behavior than the PSS data in **Figure 7.8**. Much larger frequency shifts are observed for the PAA multilayering while dissipation shifts remain low throughout. This indicates PAA layers are effectively rigid at high layer deposition numbers, in contrast to the PSS layers which continue to present soft, viscoelastic features throughout the multilayering steps. Again, the branched BGNP and star PDMAEMA display larger adsorption during each step than the linear PDMAEMA.

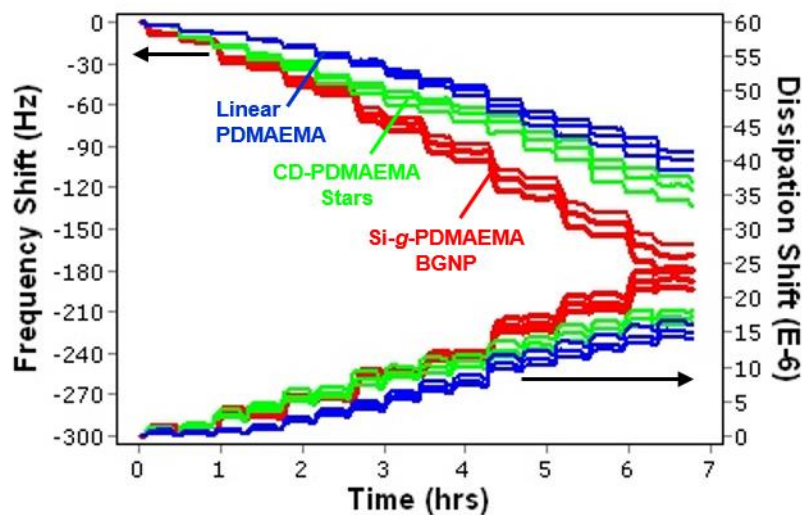


Figure 7.8. Layer-by-layer adsorption of PDMAEMA polymers with linear PSS ($M_w = 70,000$) in 1 mM NaCl, pH 5.0. Three PDMAEMA constructs are employed as the polycation: linear PDMAEMA (blue), star PDMAEMA (green), and BGNP PDMAEMA (red). The frequency shifts, $\Delta f_n/n$, and dissipation shifts, ΔD_n , are shown for the $n = 5, 7$, and 9 overtones. Adsorption is alternated between the two species, with rinsing in between steps.

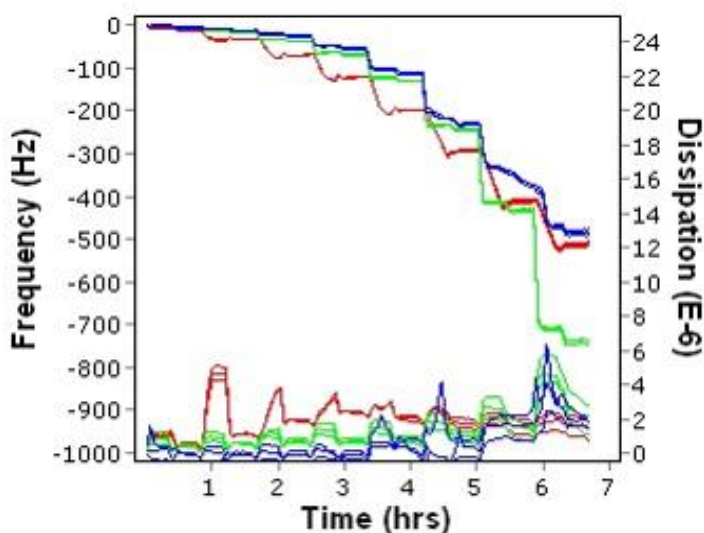


Figure 7.9. Layer-by-layer adsorption of PDMAEMA polymers with linear PAA ($M_w = 20,000$) in 1 mM NaCl, pH 5.0. Three PDMAEMA constructs are employed as the polycation: linear PDMAEMA (blue), star PDMAEMA (green), and BGNP PDMAEMA (red). The frequency shifts, $\Delta f_n/n$, and dissipation shifts, ΔD_n , are shown for the $n = 5, 7$, and 9 overtones. Adsorption is alternated between the two species, with rinsing in between steps.

Analysis of the QCM-D data for PSS and PAA multilayering with the various PDMAEMA constructs is presented in **Figure 7.10**. The adsorbed polymer mass is calculated for the PSS multilayers using the appropriate Voigt modeling, while PAA adsorbed amount is calculated by the Sauerbrey method due to the effectively large layer rigidity indicated by the low dissipation shifts.

Additionally, data is shown for multilayering of BGNP and Star PDMAEMA with Star PEO. BGNP PDMAEMA/Star PEO multilayering was discussed in the previous section, but is presented here as well for comparison. The first observation is that PAA exhibits an exponential growth curve for all three PDMAEMA polymers, while PSS exhibits a linear growth curve for all three PDMAEMA polymers. Exponential and linear are known to be the two prominent growth behaviors for polyelectrolyte multilayers¹¹, and differences in the growth modes are attributed to dynamic rearrangements of the chains within the film. Exponential growth is believed to be caused by out-of-plane diffusion³ of polymers throughout the film and entropic gains from counterion release¹² that leads to local phase separations and increased surface area. The compounding effect of increased surface area leads to this exponential type growth. Linear growth is often considered to be trademark of “stratified” multilayers where deposition of each counter polymer leads to addition of a new, discrete layer with well-defined composition. It is possible here that the fully negatively charged PSS interacts strongly with the positively charged PDMAEMA polymers, effectively creating irreversible ionic crosslinks. PAA would interact less strongly with PDMAEMA based solely on electrostatic charge regulation, thus enabling

diffusion of PAA and PDMAEMA out-of-plane and resulting in exponential film growth. The star PEO multilayers exhibit linear growth modes, but accumulate much larger masses and faster growth rates than either of the polyelectrolyte films. This is likely owing to the very high molecular weight and compactness of the star PEO microstructures and interdigitation between stars that allows very dense stratified layers to form. Comparably large frequency shifts have been attained by other star polymer multilayering strategies^{13,14}.

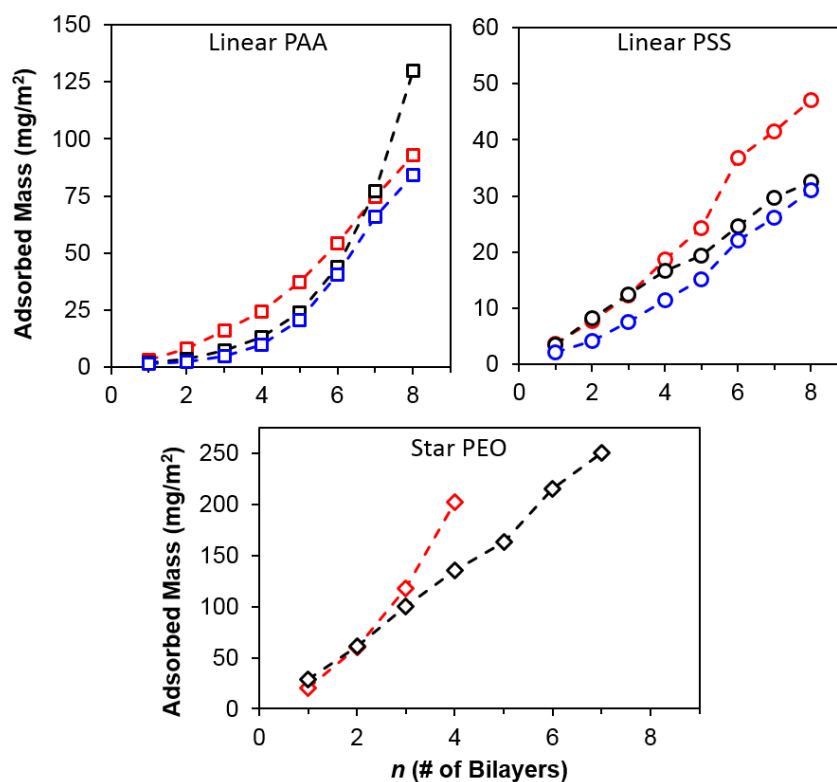


Figure 7.10. Comparison of layer-by-layer adsorption of BGMP PDMAEMA (red), star PDMAEMA (black), and linear PDMAEMA (blue) with various counter macromolecules. *Top:* Oppositely charged, linear polyelectrolytes: PAA (squares) and PSS (circles). *Bottom:* Non-ionic star PEO polymer (diamonds). PDMAEMA adsorption occurs first, followed by the counter polymer to complete each sequentially adsorbed “bilayer”. The polymers are rinsed from the bulk before switching solutions. Note differences in scale on the three ordinates.

Multilayer films are also generated and studied *ex-situ* at different multilayer deposition stages ($n = 2, 7$). The films are generated by sequential deposition from solutions onto oxidized silicon wafers. The wafers are submerged in a vial containing one polymer solution, allowed to adsorb for 20 minutes under gentle shaking, then rinsed and submerged in the counter-adsorbing polymer solution. Finally, the wafers are rinsed with de-ionized water and dried under nitrogen gas. The films are characterized in the dry state via ellipsometry, contact angle measurements, and AFM imaging. The results are tabulated in **Table 7.2**. Ellipsometry is used to assess the optical thickness of the dry layers d_{ell} . AFM images are collected and processed to obtain roughness characteristics of the films. Contact angle measurements are used finally to assess relative roughness and hydrophobicity of the dried layers. Trends in *ex situ* ellipsometry measurements of the multilayer thicknesses are consistent with *in situ* QCM-D results of swollen multilayers. The layer thickness increases from $n = 2$ to $n = 7$ for all PDMAEMA types for both PAA and PSS. Also, PAA reaches much larger thickness at $n = 7$ than PSS. The other important result is the average roughness values assessed from AFM imaging over 25 um^2 area. BGNP PDMAEMA layers tend to be rougher than linear or star PDMAEMA layers, in part due to the much larger size of BGNP PDMAEMA entities creating protrusions in the multilayers. All layers are relatively hydrophilic, displaying static contact angles with de-ionized water mostly less than 45° .

Table 7.2. Dry state characterization of oppositely charged multilayer films

	Linear PDMAEMA	Star PDMAEMA	BGNP PDMAEMA
<i>PSS, n=2</i>			
d_{ell} (nm)	2.62 $\pm$ 0.40	2.94 $\pm$ 0.11	3.51 $\pm$ 0.15
$\theta_{s,H2O}$	38 $\pm$ 1	35 $\pm$ 1	26 $\pm$ 1
R_a (nm)	0.6 $\pm$ 0.04	2.0 $\pm$ 0.05	2.2 $\pm$ 0.06
<i>PSS, n=7</i>			
d_{ell} (nm)	6.13 $\pm$ 1.9	4.60 $\pm$ 0.09	5.80 $\pm$ 0.91
$\theta_{s,H2O}$	45 $\pm$ 2	35 $\pm$ 1	29 $\pm$ 5
R_a (nm)	2.5 $\pm$ 0.18	1.9 $\pm$ 0.17	3.7 $\pm$ 0.22
<i>PAA, n=2</i>			
d_{ell} (nm)	1.49 $\pm$ 0.11	1.85 $\pm$ 0.61	1.75 $\pm$ 0.25
$\theta_{s,H2O}$	43 $\pm$ 1	41 $\pm$ 2	42 $\pm$ 2
R_a (nm)	1.1 $\pm$ 0.05	0.9 $\pm$ 0.05	1.4 $\pm$ 0.10
<i>PAA, n=7</i>			
d_{ell} (nm)	13.49 $\pm$ 1.2	11.15 $\pm$ 0.2	12.80 $\pm$ 1.2
$\theta_{s,H2O}$	48 $\pm$ 1	41 $\pm$ 1	41 $\pm$ 1
R_a (nm)	1.6 $\pm$ 0.33	1.4 $\pm$ 0.42	7.5 $\pm$ 1.40

7.2.2 Normal and lateral forces between multi-layers with linear polyanions

We have assembled a number of multilayer films on silica surfaces using PDMAEMA based polycations and both non-ionic and polyelectrolyte counterparts. The ability of a representative multilayer film to mediate surface forces is now demonstrated. The BGNP/PSS multilayer system is chosen, and colloidal probe measurements in **Figure 7.11** show force profiles for the medium coverage, patchy BGNP adsorbed layer in pH 5, 1 mM NaCl solution, as well as

the profile for the $n = 1$ “bilayer” prepared by PSS adsorption after the initial BGNP PDMAEMA adsorption. The BGNP PDMAEMA layers exhibit electrostatic repulsions at large range, and electrosteric repulsions at closer separation distances. Upon retraction, a strong bridging attraction is observed due to sub-monolayer coverages. PSS is then allowed to adsorb for 30 minutes, and after rinsing the force profile is found to be purely repulsive on approach and retraction. The repulsions are also much shorter range after the addition of negatively charged PSS to the cationic BGNP layer. This is likely caused by two factors: charge compensation due to addition of the oppositely charged PSS to the BGNP layer and BGNP brush collapse. The positive charge of the BGNPs will be reversed upon addition of PSS, resulting in a nearly net neutral adsorbed layer with little observable electrostatic repulsions. PSS also likely collapses the BGNP brush, similar to what is observed for SDS in **Chapter 6**, whereby reduced intrabrush electrostatic repulsions result in a collapsed layer. The extent to which this would occur depends on the degree of PSS penetration into the PDMAEMA brush. This was not pursued. Additionally, no bridging should be observed due to the linear nature of the BGNP PDMAEMA/PSS multilayer growth, which should result in conformal coating of the BGNPs with PSS on each bilayer adsorption sequence. Thus, residually exposed surfaces will only interact with the outermost PSS layers on each, such that no bridging attraction appears.

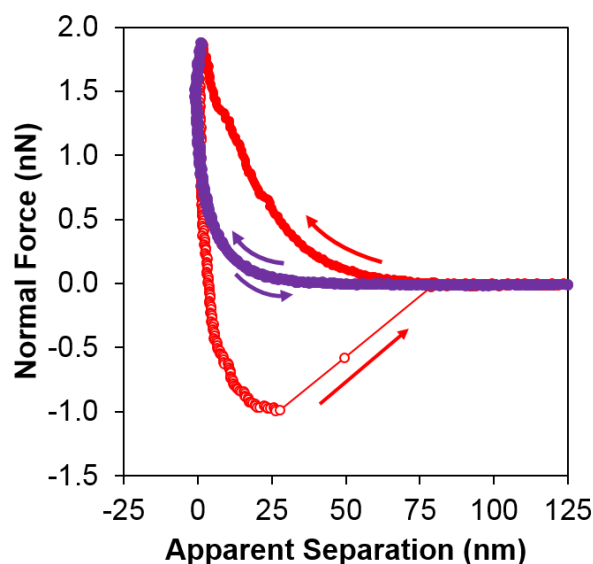


Figure 7.11. Normal force curves between a 10 μm glass probe and silica surface coated with BGNP PDMAEMA (red, adhesive) and BGNP PDMAEMA + linear PSS ($n = 1$, purple, repulsive). Background electrolyte is 1 mM NaCl, pH 5.0. Arrows indicate approach and retraction directions.

The friction versus load curves for $n = 1$ and $n = 6$ multilayers for both PAA and PSS are shown in **Figure 7.12**. Here, typical linear force vs. load behavior is observed for the $n = 2$ multilayers at low to moderate loads. However, the layers are compressed and sheared until damage results in a large jump in friction at the largest load. This wear-induced increase in friction is observed for both layers near a normal applied load of 17 – 21 nN (also report normalized force F/R that you plot) Post-friction normal force measurements exhibit adhesion after the observed wear-induced increase in frictional force, further indicating layer wear and surface exposure. However, no damage is observed when $n = 6$ multilayers are deposited and wear appears to be prevented. Instead slight deviations from linear behavior are observed, and the friction vs. load slope slightly decreases. Unfortunately, the cantilevers employed in these measurements

are relatively soft, and higher loads cannot be applied. Wear prevention is likely caused by the substantially increased layer thickness after addition of four more bilayers. The results in **Figure 7.12** prove that under these sliding conditions, multilayer films can be engineered to support both sliding and enhanced mechanical stability relative to thinner bilayer films.

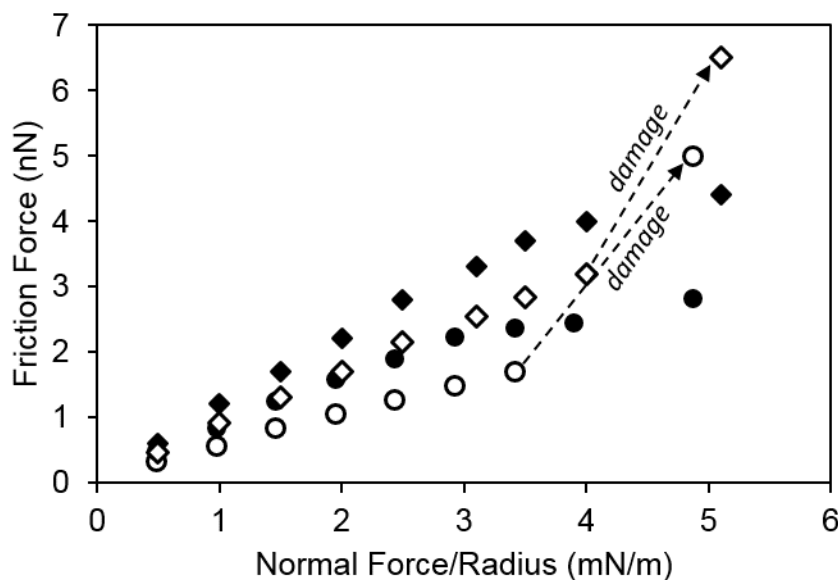


Figure 7.12. Friction versus applied load curves between a 10 μm glass probe and flat silica surface coated with $n = 1$ bilayer (open symbols) and $n = 6$ multilayer (closed symbols) of BGNP PDMAEMA with linear PSS (circles) and linear PAA (diamonds). Background electrolyte is 1 mM NaCl, pH 5.0. The dashed arrows correspond to damage conditions where large jumps in friction are observed for the $n = 1$ bilayer under high loads. Sliding speed is 5 $\mu\text{m/s}$.

7.3 Conclusions

We have successfully assembled mixed multilayer films consisting of polymer brush nanoparticles, star polymers, and linear polymers. First, the problem of bridging attraction in sparsely adsorbed PDMAEMA-grafted nanoparticle thin films is addressed by backfilling with a core-crosslinked non-

ionic star PEO polymer. Binding of the Star PEO to the BGNP PDMAEMA was observed in aqueous solution and at interfaces. Thus, sequential adsorption of Star PEO to BGNP pre-adsorbed layers leads to conformal coating of both the residually exposed silica surface and the adsorbed BGNPs. Dense packing of the Star PEO prevents bridging and results in purely repulsive normal forces as desired. The binding affinity between the two spherical polymer brushes enables multilayer assembly of thicker films. The Star PEO/BGNP mixed multilayers support smooth sliding and low coefficients of friction. Secondly, we have assembled thick multilayers using linear, star, and BGNP PDMAEMA with linear PSS and PAA. Both linear and exponential growth modes are observed using the oppositely charged polyelectrolytes at pH 5.0. Thicker multilayers can successfully prevent layer wear and damage relative to single bilayers. These two approaches demonstrate the ability for sequentially adsorbed macromolecular layers to act as boundary lubricants in aqueous environments.

7.4 References

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8. Synthesis, characterization, and surface forces between adsorbed layers of dual-responsive block star copolymers

This work details the synthesis of a series of rationally designed, water soluble star polymers with homo-, di-block, and tri-block arms using atom-transfer radical polymerization (ATRP), and the ability of these block star copolymers to adsorb at the silica/water interface and mediate surface forces. The star polymers consist of a β -cyclodextrin core with 14 arms. Copolymer arms are prepared by successive chain extension ATRP reactions. Triblock star copolymers are comprised of: 1) an inner temperature responsive non-ionic block of poly(di(ethylene glycol) methylether methacrylate) (PMEO₂MA); 2) a middle temperature and pH-responsive cationic block of poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA); and 3) a peripheral zwitterionic poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) block. The temperature response of the polymers is caused by their lower-critical solution temperature behavior in water. The non-ionic and cationic-blocks are incorporated to promote adsorption to silica surfaces and provide stimuli-responsive swelling properties, while the zwitterionic component is integrated as a lubricating block due to its strongly hydrated phosphorylcholine moieties.

The PMEO₂MA-*b*-PDMAEMA-*b*-PMPC star polymer is compared throughout to a PDMAEMA homopolymer star and the precursory PMEO₂MA-*b*-PDMAEMA diblock copolymer star. The star polymers' adsorption to silica and pH- and temperature-responsive behavior both in the bulk aqueous solution and when adsorbed are investigated here. Finally, the stimuli-responsive surface

forces are evaluated between the adsorbed star polymer layers to evaluate their frictional properties.

8.1 Synthesis of block stars via ATRP¹⁻⁶

The novel star polymers are synthesized by performing ATRP³ from cyclodextrin based initiators¹. The multifunctional cores are first synthesized, followed by a series of homopolymer stars with arms consisting of MEO₂MA, DMAEMA, or MPC. Diblock and triblock star copolymers are synthesized by successive, chain extension polymerization reactions from the homopolymer star macroinitiators. The synthesis steps are shown in **Figure 8.1** and described in detail in the section below. The targeted structures should exhibit pH- and temperature-responsive properties in water resulting from the monomers utilized. PMEO₂MA⁷ is a slightly hydrophilic, non-ionic polymer that exhibits a lower critical solution temperature in water of 25 – 30 °C. PDMAEMA is a dual-responsive polymer also exhibiting a lower critical solution temperature in aqueous solution. PDMAEMA also possesses a pH dependent degree of ionization, and this weak cationic behavior causes the LCST to be a function of pH. PDMAEMA can exhibit LCST in the range of 35 – 100 °C depending on the degree of ionization of the polymer. Finally, we will incorporate a zwitterionic PMPC into the star polymers. PMPC is very hydrophilic and displays little to no pH or temperature responsiveness in water. Ultimately, combinations of these building blocks should generate a series of star polymers that can adsorb to silica surfaces and act as multi-responsive, aqueous boundary lubricants.

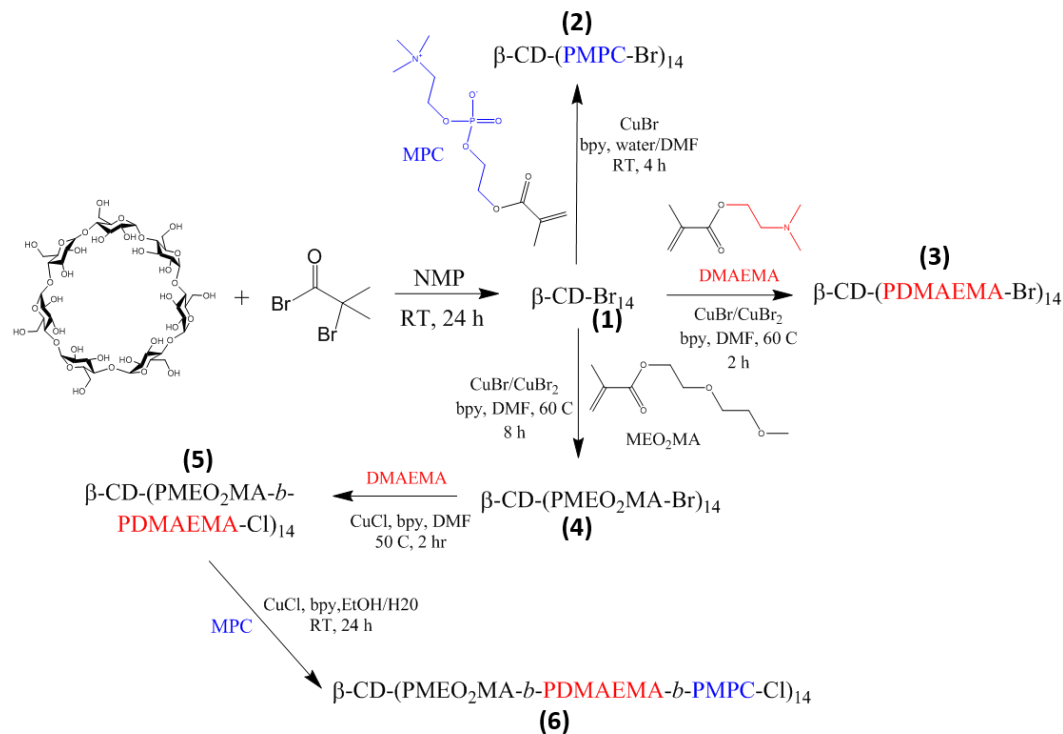


Figure 8.1. Synthesis of 14-arm star polymers from β -cyclodextrin cores.

8.1.1 Cyclodextrin initiators

(1): β -CD-14Br: 10 g of β -cyclodextrin (β -CD, 8.81 mmol) was dried under vacuum overnight and placed in a 250 mL round bottom flask. The β -CD was dissolved in 100 mL of anhydrous 1-methyl-2-pyrrolidone (NMP), and the flask was placed in an ice bath. 2-bromoisobutyryl bromide (BriBB, 27 mL, 1.2 eq. to -OH) was dissolved in anhydrous NMP (50 mL) and slowly added to the previous β -CD solution. The solution temperature was increased slowly to room temperature and allowed to stir for 1 day. The dark brown solution was dialyzed against distilled water (Spectra/Por membrane, MWCO = 500) for 1 week. Remaining product was concentrated by reduced pressure and crystallized in cold hexanes to obtain a slight yellow powder.

8.1.2 Homopolymer stars

The ATRP reaction conditions are provided below for star polymers.

Unless noted elsewhere, standard procedure involving de-gasification of all solvents and monomers and three nitrogen backfills are performed with the Schlenk flask prior to initiating the reaction.

(2): β -CD-(PMPC): β -CD-14Br (0.02 g), MPC (80 eq. per Br, 2 g), CuBr (0.012 g), bpy (0.027 g) and 20 mL DMF/water (1:1, v:v). The reaction proceeds at room temperature. The reaction is stopped by exposure to air. The mixture is transferred to dialysis tubing (Spectra/Por, MWCO 15000) and purified against water for 3 days.

(3): β -CD-(PDMAEMA): β -CD-14Br (0.4 g, 0.118 mmol), DMAEMA (100 eq. per Br, 26.0 g, 1.652 mmol), CuBr (0.118 g, 0.826 mmol), bpy (0.258 g, 1.65 mmol), and 28 mL of DMF are heated to 50 °C for 2 hours. The reaction is stopped by exposure to air. The mixture is transferred to dialysis tubing (Spectra/Por, MWCO 15000) and purified against methanol/water for 3 days.

(4): β -CD-(PMEO₂MA): β -CD-14Br (0.4 g, 0.118 mmol), MEO₂MA (150 eq. per Br, 247.8 mmol, 46.6 g), CuBr (0.095 g, 0.661 mmol), CuBr₂ (0.037 g, 0.165 mmol), bpy (0.103 g, 0.661 mmol) and 91 mL DMF are heated to 60 °C and the reaction proceeds for 8 hours. The reaction is stopped by exposure to air. The mixture is transferred to dialysis tubing (Spectra/Por, MWCO 15000) and purified against methanol/water for 3 days.

8.1.3 Diblock star

(5): β -CD-(PMEO₂MA-*b*-PDMAEMA): CD-PMEO₂MA-Br (5 g), DMAEMA (100 eq. per Br, 8.2 g), CuCl (0.05 g), bpy (0.17 g) and 9 mL DMF/water (1:1, v:v). The reaction proceeds at 60 °C for 2 hours. The reaction is stopped by exposure to air. The mixture is transferred to dialysis tubing (Spectra/Por, MWCO 15000) and purified against methanol/water for 3 days.

8.1.4 Triblock star

(6): β -CD-(PMEO₂MA-*b*-PDMAEMA-*b*-PMPC): 1.0 g of β -CD-(MEO₂MA-*b*-DMAEMA-Cl)₁₄ macroinitiator is placed in a 20 mL vial with 8 mL of ethanol/water (1:2, v:v) mixture and stirred until dispersed. 1.48 g of MPC are dissolved in 3 mL of water/ethanol. Monomer and macroinitiator solutions are added to a Schlenk flask and bubbled with nitrogen for 20 minutes. 0.0067 g of CuCl, 0.021 g of bpy, and 2 mL of ethanol/water are placed in a vial, bubbled with nitrogen for 20 minutes and stirred until dissolved. CuCl/bpy solution is added to the Schlenk flask and the reaction mixture stirred at room temperature for 24 hours. The reaction is stopped by exposure to air. The mixture is transferred to dialysis tubing (Spectra/Por, MWCO 15000) and purified against methanol/water for 3 days and against water for 3 days. The product is dried to yield a clear to slightly cloudy plastic solid.

8.2 Characterization of star polymers

The novel star polymers synthesized above were characterized to assess their relative compositions, molecular weight, and aqueous solution properties. The preliminary characterization presented here is not comprehensive, and work in

determining the absolute molecular weight and more detailed properties are underway in the project of Wenjie Wu, a MS student in Chemical Engineering. Nevertheless, the expected polymer compositions and architectures are confirmed and their physical properties relevant to surface forces are presented here.

8.2.1 Structural characterization

The degree of polymerization (DP) of each homopolymer star and each block of the di- and tri-block star polymers are summarized in Table 8.1. The degree of polymerization is the number of monomers that have been successfully polymerized and incorporated into the star polymers. DP of the stars is measured by ^1H -NMR. The area under the vinyl peak associated with each methacrylate-based monomer is proportional to the concentration of monomer in solution. NMR spectra obtained before and after polymerization show a decrease in the vinyl peak area, and the ratio of the areas is taken to be the *conversion* of monomer. Multiplying the conversion by the initial concentration of monomer used allows the calculation of DP. The theoretical molecular weight of the star polymer can be calculated from the molecular weight of the core, the arm number f , and the molecular weight of each arm:

$$M_w = M_{w,\beta\text{-CDBr}} + f M_{w,arm}$$

$$M_{w,arm} = \sum_{i=A}^C M_{w,i} DP_i \quad (8.1 - 2)$$

The molecular weights of the monomers are: MEO₂MA (188.2 g/mol), DMAEMA (157.2 g/mol), and MPC (295.3 g/mol). The molecular weight of the initiator functionalized β -cyclodextrin is 3220 g/mol.

Table 8.1. Composition of star polymers.

Sample ID ⁱ	DP-A ⁱⁱ	DP-B ⁱⁱ	DP-C ⁱⁱ	$M_{w,theo}$
(2)	55	---	---	230,578
(3)	45	---	---	102,269
	62			139,687
(4)	50	---	---	134,960
(5)	50	35	---	211,998
(6)	50	35	17	282,272

(i): labeled according to Figure 8.1. (ii): DP calculated by $^1\text{H-NMR}$ of vinyl monomer peaks before and after polymerization.

Traditional GPC cannot be used to confirm the absolute molecular weight of the star polymers because this method is calibrated using linear polymer standards. The elution times measured for star polymers using traditional GPC will not predict the proper elution time because the excluded volume interactions between stars and the chromatography column are not the same as linear random-coil polymers. Thus, we are in the process of characterizing the absolute molecular weight of the star polymers using static light scattering. Static light scattering is an optical method, and with knowledge of the optical properties of the polymer can be used to determine size, molecular weight, and second virial coefficient of polymer solutions. This work is underway in the MS research of Wenjie Wu, however preliminary static light scattering measurements on the triblock star polymer are given in **Figure 8.2** in the form of a Zimm plot. Zimm analysis confirms that the triblock star polymer has a high molecular weight, M_w

$= (6.79 \pm 0.31) \times 10^5$. The measured M_w is approximately three times higher than the theoretical molecular weight in **Table 8.1**. It is possible that multi-star aggregates with a low aggregation number of 2 -3 have formed, resulting in a higher than expected molecular weight. The radius of gyration also suggests that aggregation may have occurred. The measured $R_g = 93.3 \pm 4.1$ nm is substantially higher than the measured hydrodynamic size of the particles discussed later. However, R_g measured here is likely a more accurate measure of size than the hydrodynamic radius owing to the model used to interpret DLS data. Static light scattering of the remaining polymer solutions under various temperatures and pH will elucidate further detailed structural information about the star polymers. It is likely that this triblock star assumes a conformation similar to a core-shell polymeric nanoparticle. In the schematic depiction, the PMEO₂MA inner block is poorly solvated and forms a collapsed core, and the cationic and zwitterionic blocks protrude as expected for well-solvated star arms.

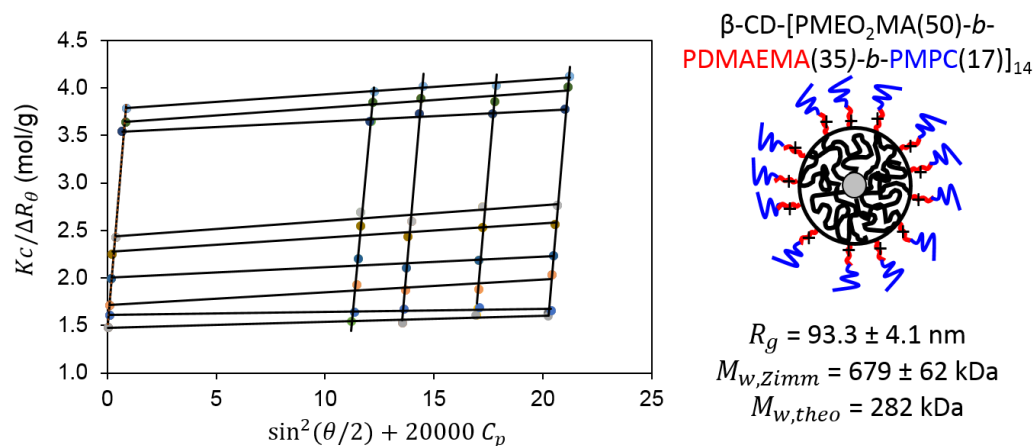


Figure 8.2. Static light scattering Zimm analysis of triblock star polymers at pH 5.0 in 1 mM NaCl. The regression results for the radius of gyration and absolute molecular weight of the triblock star polymer are given, and the theoretical molecular weight based on degree of polymerization.

8.2.2 Effect of pH on size and ionization of star polymers in aqueous solution

The inclusion of PDMAEMA imparts pH-dependent properties unto the star polymers. PDMAEMA has a pK_a of 7.0 – 7.5 in aqueous solution⁸ and the dimethylamine groups in the polymer are more protonated at low pH than at high pH. Thus, the polymer becomes less positively charged as solution conditions go from acidic to basic, approaching neutrality at high pH. The degree of protonation plays an important role on the solution properties of PDMAEMA, including the size of the polymer and the polymer's stability with respect to aggregation. Also, the positive charge on PDMAEMA will drive adsorption of the star polymers to negatively charged surfaces, and the adsorbed layer conformation will depend strongly on the pH, as is usually the case for weak polyelectrolyte adsorption⁹.

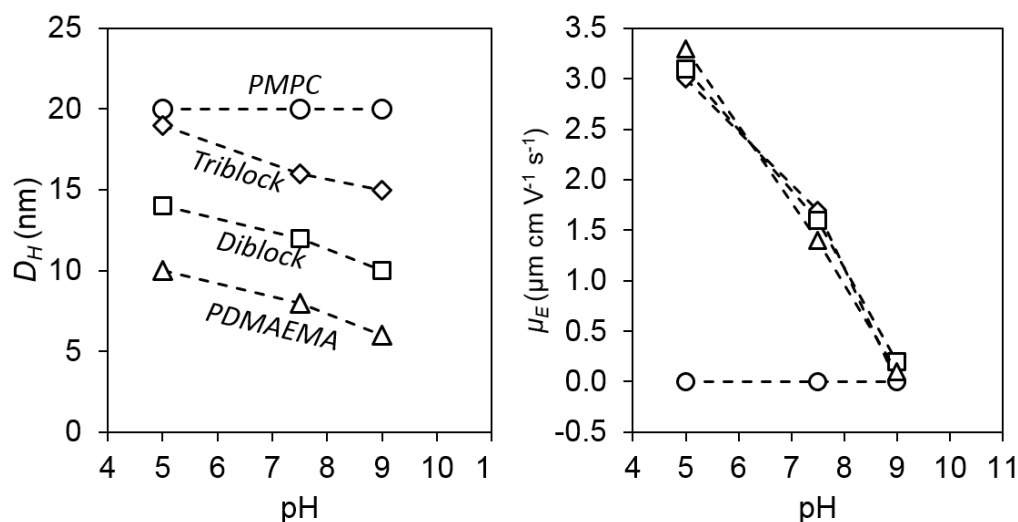


Figure 8.3. Swelling and ionization of 14-arm star polymers in 10 mM NaCl aqueous solution as a function of pH. β -CD-[(PMPC(54))₁₄] (circles), β -CD-[(PDMAEMA(45))₁₄] (triangles), β -CD-[(PMEO₂MA(50)-*b*-PDMAEMA(35))₁₄] (squares), β -CD-[(PMEO₂MA(50)-*b*-PDMAEMA(35)-*b*-PMPC(17))₁₄]. *Left*: Number-average hydrodynamic diameter measured by dynamic light scattering. *Right*: Electrophoretic mobility measured by electrophoretic light scattering.

The effect of pH on the size and charge of various star polymers is shown in **Figure 8.3**. Here, the star polymers containing PDMAEMA are characterized via dynamic and electrophoretic light scattering at pH 5.0, 7.5, and 9.0. The hydrodynamic diameter presented here is inferred from the measured diffusion coefficient via the well-known Stokes-Einstein equation. This model accurately represents hard spheres, but for other structures, such as soft, permeable star polymers, it provides the size of the hydrodynamically equivalent sphere. Thus the quantitative size measurements should not be interpreted as a physical dimension of the star polymers, rather as used here to demonstrate qualitative size changes with respect to pH. The measured electrophoretic mobility is model-independent. The zwitterionic PMPC homopolymer star is also included since it does not contain PDMAEMA. The PMEO₂MA homopolymer stars are not shown here due to their aggregation and formation of a turbid solution at 25 °C, preventing isolated stars from being measured.

PMPC stars display a constant hydrodynamic diameter of approximately 20 nm across the entire pH range of 5 to 9. PMPC stars also have an electrophoretic mobility of zero, indicating that they are net neutrally charged and do not gain translational velocity in response to an applied electric field. pH effects are observed for each of the PDMAEMA-containing star polymers: PDMAEMA homopolymer star, MEO₂MA-*b*-DMAEMA diblock star, and MEO₂MA-*b*-DMAEMA-*b*-MPC triblock stars all decrease in size and electrophoretic mobility with increasing pH. Each of these three star polymers is strongly positively charged at pH 5.0, reduce in charge at pH 7.5, and approach

neutrality at pH 9.0. The PDMAEMA-containing polymers also decrease in size as pH increases due to reduced segment-segment electrostatic repulsions that tend to swell the star polymers. These experiments highlight the successful incorporation of PDMAEMA into the homopolymer, diblock, and triblock stars and the importance of pH for the conformation and swelling of the structures in aqueous solution.

8.2.3 *Thermally-induced aggregation in aqueous solution*

Having confirmed the pH-responsiveness of the star polymers containing PDMAEMA, we next investigated the temperature responsive properties. The LCST behavior of the star polymers is assessed by monitoring the transmission of 500 nm light through 1.0 mg/mL polymer solutions during heating and cooling. The attenuation light due to scattering is referred to as the “optical density” of the solution and its mathematical definition is equivalent to absorbance. OD increases correspond to aggregation in the polymer solution, and large OD increases (~1-2 OD units) are indicative of a solution transition from clear to turbid. The temperature at which this occurs is referred to as the cloud point temperature of the star polymer solutions, and is closely related to the LCST of the polymers. The star architecture reduces the configurational degrees of freedom of the polymers relative to a linear chain, which tends to cause deviation in cloud point from what would be observed for the equivalent linear polymer.

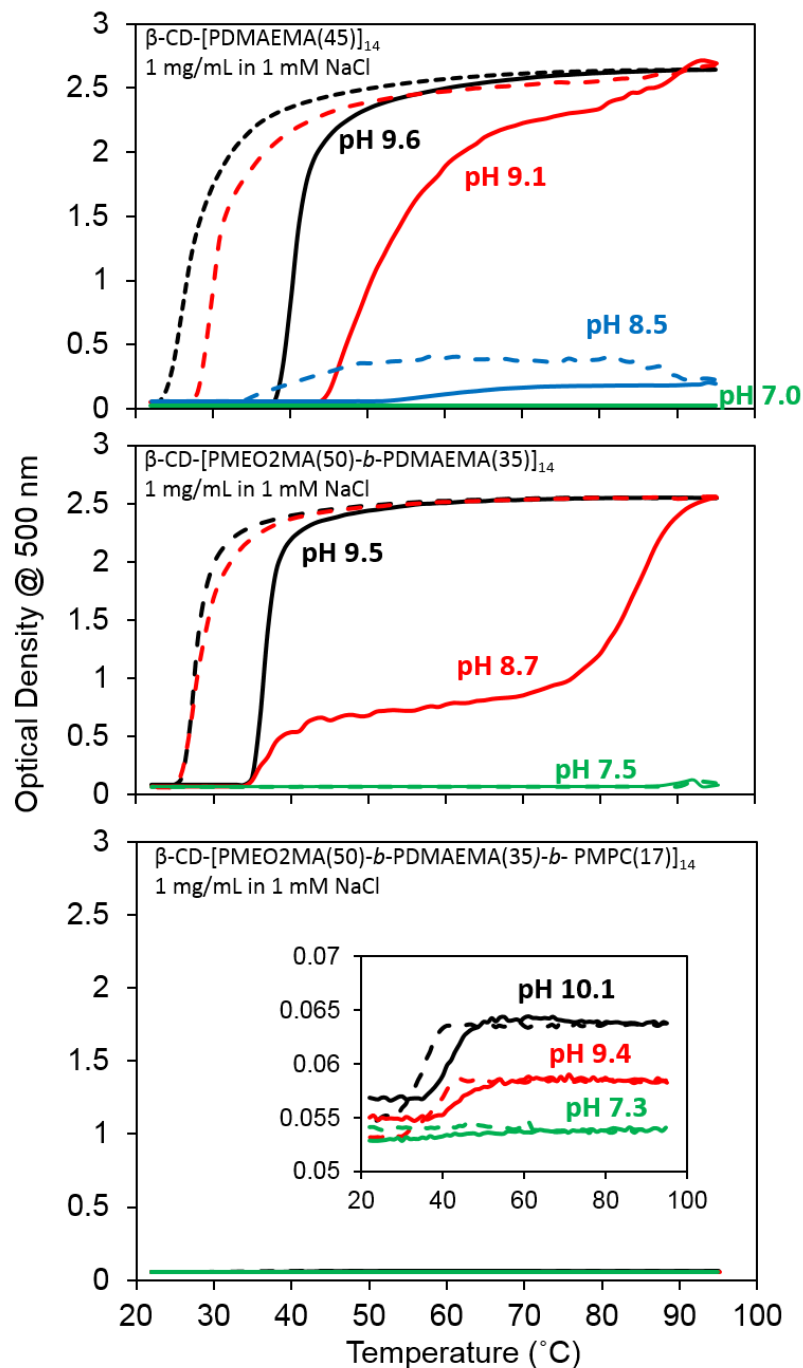


Figure 8.4. Turbidity of 1.0 mg/mL star polymer solutions during heating (solid lines, 2°C/min) and cooling (dashed lines, 3°C/min) cycles. The optical density, or relative amount of scattered light at a wavelength of 500 nm, is measured as a function of pH and temperature on a UV-Vis spectrophotometer. *Top:* homopolymer PDMAEMA stars. *Middle:* diblock MEO2MA-*b*-DMAEMA stars. *Bottom:* triblock MEO2MA-*b*-DMAEMA-*b*-MPC stars, with inset providing a zoomed in view of apparent small-scale microstructural changes in the triblock data.

The stability of star polymer solutions during heating and cooling is shown in **Figure 8.4**. Stability measurements are performed for the homopolymer PDMAEMA star, diblock PMEO₂MA-*b*-PDMAEMA star, and triblock PMEO₂MA-*b*-PDMAEMA-*b*-PMPC star polymers as a function of pH. The PDMAEMA homopolymer stars exhibit the lowest cloud point temperature at high pH. The cloud point temperature increases as pH decreases as the PDMAEMA arms become more strongly positively charged. Increased ionization is analogous to improving solvent quality of the polymer in water, since water will interact more favorably with charged monomers than uncharged. The electrostatic repulsion between positively charged arms at pH 7.0 is sufficient to prevent thermally-driven LCST-type aggregation of the homopolymer stars. With an understanding of the homopolymer PDMAEMA star thermal response, we probe the stability of diblock PMEO₂MA-*b*-PDMAEMA star polymers. The PDMAEMA stars can be re-dispersed by cooling the polymer solution, but the process is not fully reversible. The PDMAEMA stars must be cooled to a lower temperature to transition from large aggregates to fully re-dispersed stars. This hysteretic process of re-dispersing micron sized star polymer aggregates is not well understood.

The diblock stars consist of a peripheral PDMAEMA block, but now have an inner PMEO₂MA block emanating directly from the cyclodextrin core. The pH-dependent LCST behavior is shown for the PDMAEMA homopolymer. PMEO₂MA is a non-ionic polymer with an LCST of 25 – 29 °C in water. Thus, the diblock star is an example of a dual-transition polymer and this behavior is

captured in the cloud point measurements of **Figure 8.4**. At pH 9.5, the outer PDMAEMA block is de-protonated and a single effective cloud point temperature is observed near 35 °C. However, two transitions are observed when the pH is decreased to 8.7: a primary transition temperature at 35 – 40 °C and a secondary transition temperature at 75 – 85 °C. This behavior indicates that the diblock polymer first undergo a microstructural aggregation process that yields a relatively stable, or self-limiting, aggregate at intermediate temperatures. These aggregates then undergo a further thermally induced aggregation into larger, more turbid microstructures at the higher temperature. The lower temperature transition is likely driven by the PMEO₂MA inner blocks, creating micellar or other self-assembled structures that maximize PMEO₂MA- PMEO₂MA segment contacts until limited by the outer, solvated PDMAEMA blocks. Further heating above the PDMAEMA LCST allows the remaining blocks to aggregate and form large scale flocs. Dropping the pH to 7.5 charges the PDMAEMA blocks enough to prevent the formation of large scattering entities, with the exception of a small OD increase at 92 °C. Importantly, partial ionization appears to prevent the primary PMEO₂MA-driven aggregation transition from occurring at low temperatures.

The triblock stars display a sharp departure from the cloud point behavior of the homopolymer and diblock star solutions. No large-scale aggregation is observed for the triblock stars. This indicates that the addition of short, but strongly hydrophilic PMPC blocks to the end of the diblock stars provides a sufficient steric barrier to prevent the formation of large aggregates that strongly scatter light. Even at pH 10.1, where PDMAEMA is fully de-protonated and de-

swollen, no large OD increases are observed. Closer inspection of the high pH curves identifies very small OD jumps ($\sim 0.005 - 0.01$) upon heating and cooling of the triblock stars. These jumps are small but measureable outside of the instrument noise, suggesting that they are real effects. The triblock stars still possess the two temperature responsive blocks, and it is possible that some small, multi-star aggregates – possibly micelles – form upon heating, similar to block copolymer and other amphiphiles. It is also possible that the collapse of the inner blocks to a more condensed state slightly increases scattering due to a higher effective refractive index. The observation that large aggregates are not formed is significant and opens the possibility that pH and temperature can be used to independently tune the size and hydration of the inner PMEO₂MA and PDMAEMA blocks while primarily maintaining individually dispersed stars.

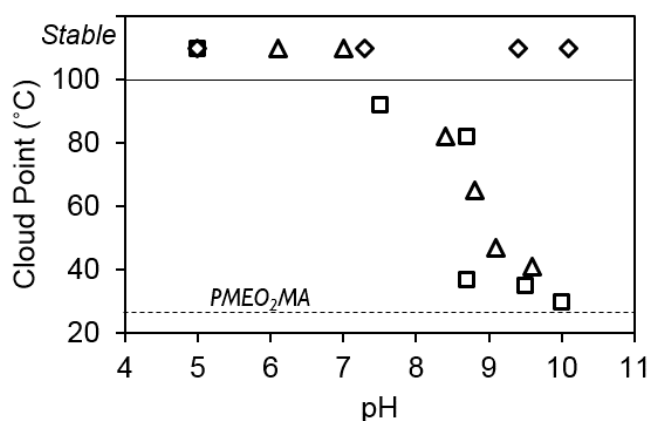


Figure 8.5. Cloud point temperature of 1.0 mg/mL star polymer solutions in 1 mM NaCl determined optical density measurements in Figure 8.4. Homopolymer PDMAEMA stars (triangles), diblock MEO₂MA-*b*-DMAEMA stars (squares), triblock MEO₂MA-*b*-DMAEMA-*b*-MPC stars (diamonds). Heating cycles only reach 100 °C and samples that exhibit no large-scale aggregation are marked “stable” and plotted arbitrarily above the 100 °C line. The pH-independent cloud point for linear PMEO₂MA¹⁰ is represented by the dotted line at 27 °C. Note: The diblock star exhibits two transition temperatures at pH 8.7.

The measured cloud point temperature for the star polymers as a function of pH are summarized in **Figure 8.5**. Conditions that resulted in no aggregation in the temperature range 25 – 100 °C are marked as “stable” in the figure. The cloud point temperature changes the most drastically for the homopolymer PDMAEMA stars and diblock stars at $\text{pH} > \text{pK}_a$ (7.5), which is expected for nanoparticles electrostatically stabilized by weak cationic groups and weak polycations. The ability to tune star polymer stability in aqueous solution using temperatures of 29 to greater than 90 °C, further modulated by pH, provides a broad operating space for formulating responsive star polymer solutions and adsorbed layers. Further characterization of the aggregate microstructure above the cloud point is required to gain a better understanding of the associative, star polymer assembly mechanisms.

8.3 Adsorption and surface forces between star polymer layers

8.3.1 Adsorption measured by QCM-D

The star polymers are expected to adsorb strongly to silica, although each monomer type should interact with the surface through different mechanisms. MEO₂MA contains EO units capable of hydrogen bonding to silanol groups at silica surfaces. This is analogous to PEO adsorption, which has been discussed in detail in **Chapters 3 and 7**. MEO₂MA core-crosslinked star polymers have been shown previously by the Matyjaszewski group and collaborators² to form thermoresponsive films when spin-coated on wafers, indicating favorable interactions between the polymer and surface. It is also possible that hydrophobic interactions between the methacrylate backbone or pendant methyl moieties could

also contribute to MEO₂MA adsorption on silica. DMAEMA will adsorb to silica through electrostatic interactions between positively charged monomer groups and negatively charged, dissociated silanol groups. The electrostatic aspects of linear PDMAEMA and PDMAEMA brush-grafted nanoparticle adsorption to silica have been discussed in detail in **Chapter 4**. Even MPC is likely to interact favorably with silica surfaces. Phospholipids have been known for decades to form supported lipid bilayers on silica surfaces, with the hydrophilic, phosphoryl choline head groups interfacing with the surface¹¹. The combination of all three polymer entities in the triblock star polymer may impart strong surface activity and robust, synergistic adsorption under a variety of conditions, yielding layers that are dually responsive to pH and temperature.

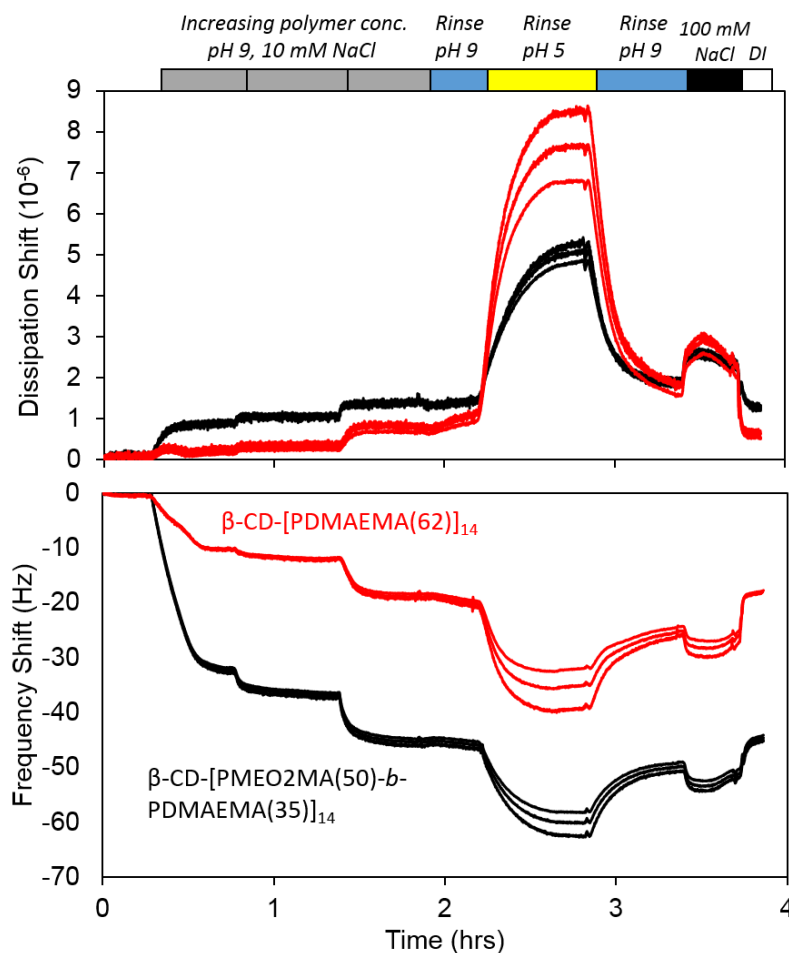


Figure 8.6. In situ QCM-D measurements of star polymer adsorption on silica surfaces. Frequency and dissipation shifts are shown for the 5th, 7th, and 9th overtone numbers. The experimental sequence and duration of each step is provided at the top, starting from initially bare surfaces in 10 mM NaCl at pH 9.0. Polymer concentration increases from 0.001 to 0.01 to 0.1 mg/mL, followed by a polymer-free rinse in 10 mM NaCl. Then, the adsorbed layer is subjected to 10 mM NaCl rinses to pH 5.0 and pH 9.0 to swell and then de-swell the layer. Finally, adsorption is challenged with 100 mM NaCl and salt-free rinses. Note: a slightly higher molecular weight PDMAEMA star is employed here.

The adsorption of PDMAEMA homopolymer star and PME02MA-*b*-PDMAEMA di-block star polymers on silica is shown in **Figure 8.6**. Here, the star polymers are initially adsorbed at pH 9 – near their isoelectric point to promote a high surface excess concentration of polymer to adsorb. Recall, silica

bears a strong negative charge at pH 9.0, thus a larger amount of star polymer will adsorb in order to compensate the surface charge of the substrate. This surface charge compensation is balanced with entropic losses incurred by the adsorbing polymer. The adsorbed layer is formed through step-wise increases in the bulk polymer concentration, from 0.001 – 0.1 mg/mL. The magnitude of the negative frequency shift and the dissipation increase for each of the concentration increments, indicating that the surface is becoming more saturated with polymer. Adsorption is higher for the di-block star than the homopolymer star, representing their larger molecular weight per unit area of adsorbed star polymer. Next, the polymers are rinsed from the bulk at constant ionic strength and pH (10 mM NaCl, pH 9.0). The magnitudes of the frequency and dissipation shifts do not decrease upon polymer-free rinse, demonstrating the irreversible adsorption of the stars onto silica. The slight drift in the star PDMAEMA layer is likely due to slight pH imbalance between the solvents.

The adsorbed layers are then subjected to changes in pH at a constant ionic strength to test their surface swelling properties. Upon rinsing the layers to pH 5.0, the dissipation shift rapidly increases and the frequency shift increases in magnitude, consistent with an increased bound mass. Since no additional polymer is available for adsorption, this additional mass must be trapped water. This suggests that the layer is swelling in response to the pH decrease. Swelling of PDMAEMA is expected at pH 5 due to the protonation of monomers. Additionally, the surface charge of the underlying substrate decreases when changing from pH 9 to pH 5. Given the strong likelihood of adsorption hysteresis,

there will be a larger amount of polymer trapped on the surface than is required to compensate the lower surface charge density at pH 5, thus the layer will swell in order to extend the excess charged segments as far away from the surface as possible. It is important to also remember that QCM-D dissipation and frequency shifts include contributions from the adsorbed polymer layer *and* any hydrodynamically coupled solvent, thus changes in the relative layer hydration will result in changes in the QCM-D signals. The layers also de-swell upon rinsing solution conditions back to pH 9.0. This de-swelling is caused by the de-protonation of PDMAEMA in the star polymers, and the resulting change in layer conformation and water content. The evidence for swelling and de-swelling of the layers in QCM-D confirms that the star polymers maintain a similar pH-responsive behavior at the surface as is observed in the bulk polymer solution via light scattering. The relative swelling and de-swelling is stronger for the PDMAEMA homopolymer star compared to the diblock star. This is likely due to the larger PDMAEMA content in the adsorbed homopolymer star layer. Also, the entire PDMAEMA homopolymer star will adjust to respond to the pH changes, whereas the 50 unit PMEO₂MA inner block of the di-block star possesses no pH-responsiveness. Both adsorbed star polymer layers persist through 100 mM NaCl and salt-free rinses, indicating their robustness and strong binding at the surface.

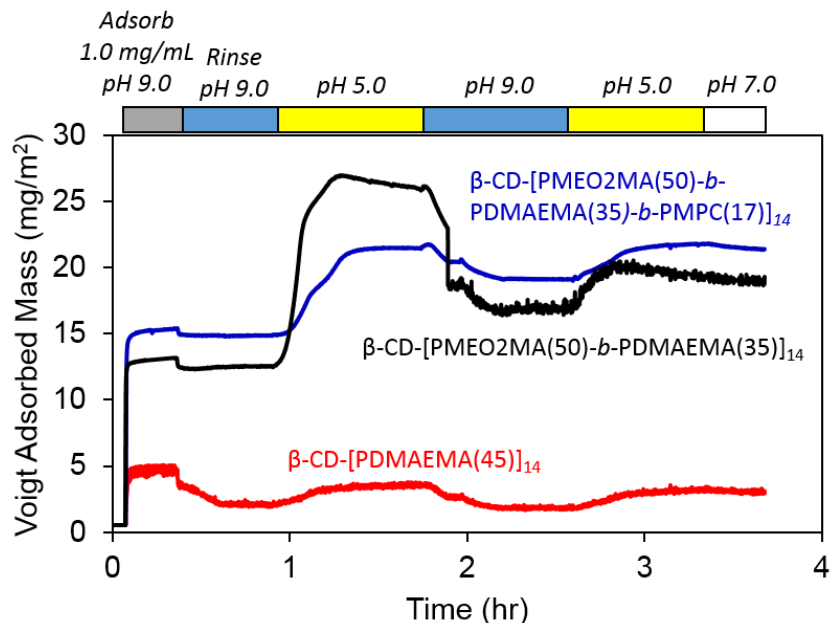


Figure 8.7. QCM-D adsorption measurements comparing adsorption and pH-induced swelling/de-swelling of homopolymer, di-block, and triblock star polymers. All measurements are in 10 mM NaCl. Data has been modeled using the Voigt viscoelastic model. Initial adsorption occurs from 1.0 mg/mL polymer solutions at pH 9.0, followed by polymer-free rinse. The adsorbed layers are then subjected to pH-cycles that cause layer swelling and de-swelling.

A separate adsorption experiment comparing the pH-responsiveness of homopolymer, diblock, and triblock star polymer adsorbed layers is shown in **Figure 8.7**. Here, the data is presented as the “Voigt mass” determined by fitting the data to the Voigt viscoelastic layer model. Additionally, the star polymers are adsorbed at an initial concentration of 1.0 mg/mL to ensure that they are formed on the adsorption plateau of the isotherm. We see that the triblock star polymer adsorbs to a slightly higher extent than the diblock, and both are significantly higher than the PDMAEMA homopolymer star. Again, all three polymers display the expected pH-responsive swelling behavior during a rinsing sequence that includes two cycles changing from pH 9.0 to pH 5.0 and a final rinse to the

intermediate pH of 7.0. Interestingly, the Voigt mass after swelling at pH 5.0 and subsequently de-swelling at pH 9.0 remains higher than the initial adsorbed layer that is formed by adsorption at pH 9.0. This suggests an irreversible layer conformation change that occurs in addition to the reversible, pH-mediated swelling and de-swelling. Additional adsorption can be ruled out because all the bulk material has been rinsed away.

8.3.2 *Miscellaneous star polymer adsorption observations*

Adsorption of homopolymer PMPC stars on silica is tested in **Figure 8.8**. Adsorption of PMPC stars on silica at pH 9.0 at concentrations of 0.001 and 0.01 mg/mL, in 10 mM NaCl. Here, PMPC is injected at a concentration of 0.001 mg/mL and pH 9.0. Small frequency and dissipation shifts are observed for the lowest polymer concentration (0 – 0.25 h). Larger frequency and dissipation shifts are realized when the bulk polymer concentration is increased to 0.01 mg/mL, indicating the formation of a PMPC star adsorbed layer. This layer shows no desorption upon rinsing with polymer free 10 mM NaCl solution at 1.4 hrs. Adsorption of the PMPC stars is likely caused by interactions between the phosphoryl choline groups and the silica surface. Common phosphoryl choline-based lipids, such as DPPC and DMPC, are known to form supported lipid bilayers on silica and glass¹². The zwitterionic headgroups interface with the silica surface in the supported lipid bilayers, and the adsorption behavior seen here for PMPC stars is probably driven by the same interactions believed to support lipid bilayer formation. The attraction is attributed to van der Waals and electrostatic

forces, which typically provide reasonable surface-headgroup separation distances. The observation that PMPC interacts favorably with silica has important implications for surface force measurements. Zwitterionic polymers have gained interest in recent years following a few reports of the remarkable, low-friction lubrication properties of high-grafting density zwitterionic polymer brushes^{4,13}. However, if the adsorbed layers here do not mimic a “high-grafting density” brush layer, then the possibility of PMPC bridging arises. This undermines the low-friction, hydration lubrication mechanism proposed for interacting zwitterionic brushes¹⁴. It is notable that supported lipid bilayers have been shown to display significant lateral diffusivity, and some authors have attributed this to low friction between the zwitterionic headgroup and surface¹⁵. This may result in low friction forces in spite of bridging.

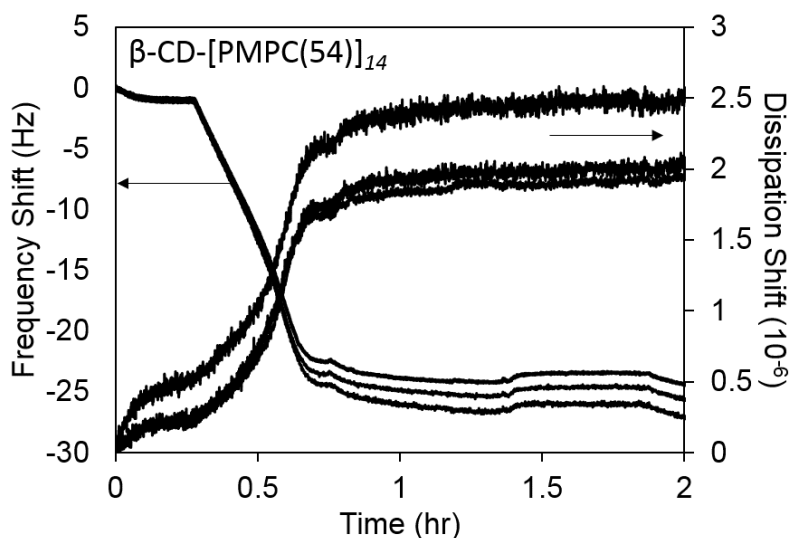


Figure 8.8. Adsorption of PMPC stars on silica at pH 9.0 at concentrations of 0.001 and 0.01 mg/mL, in 10 mM NaCl.

Another interesting aspect that merits discussion is the adsorption of PDMAEMA homopolymer stars on silica *above cloud point*. A brief discussion of temperature effects with respect to PDMAEMA-grafted nanoparticles is provided in **Chapter 4**, but the discussion is limited to temperatures approaching but remaining below the suspension flocculation temperature. Ultimately, temperature processing of PDMAEMA-grafted nanoparticles resulted in adsorption hysteresis with respect to temperature and excess brush nanoparticle adsorption on the surface relative to the amount of adsorption that would be produced by direct adsorption at lower temperatures. This was likely caused by driving the polymers that are in contact with the surface to collapse on heating, bringing more monomers into contact with surface. Upon cooling and attempted re-swelling, the near-surface re-swelling is kinetically-hindered from the strong multi-segment contact, preventing particles from desorbing in a reversible fashion.

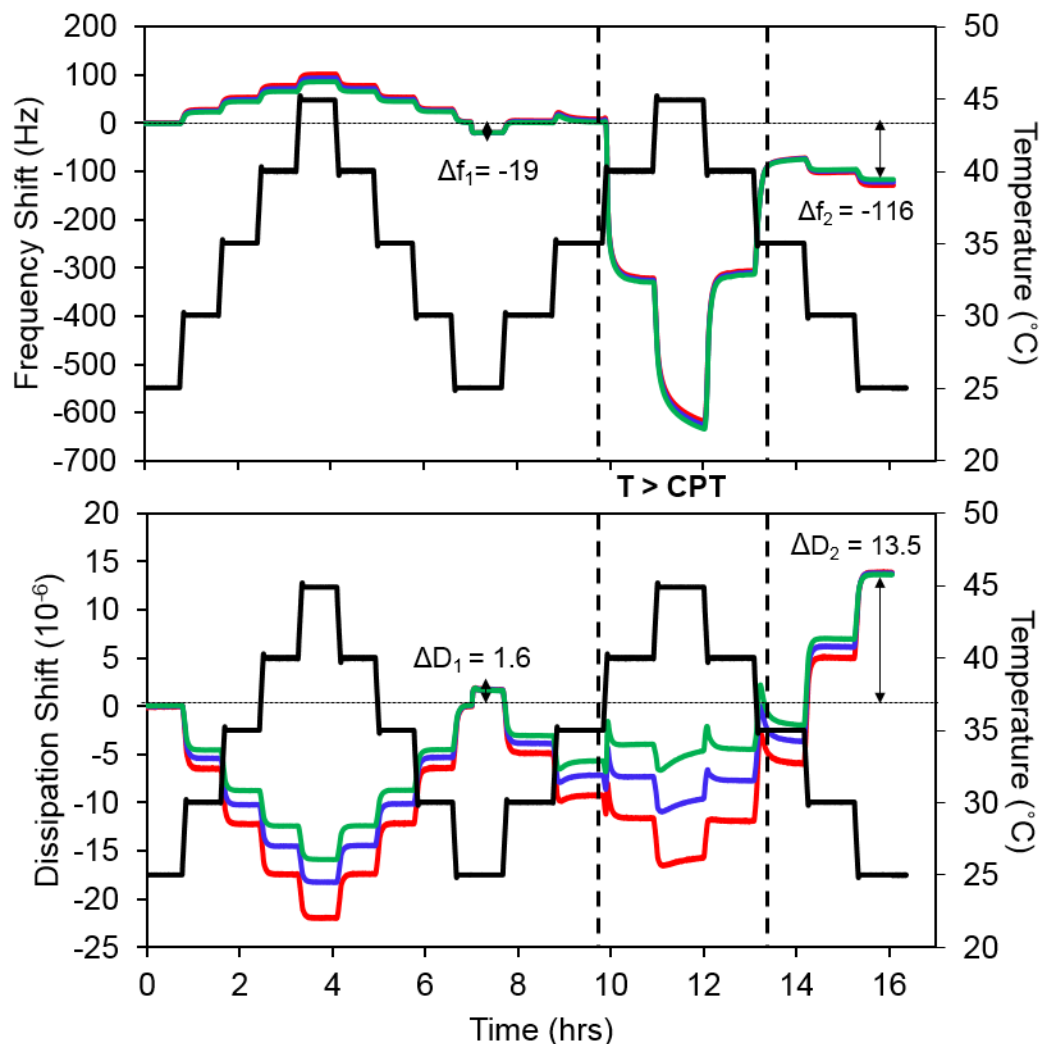


Figure 8.9. QCM-D adsorption of PDMAEMA homopolymer stars from a 0.1 mg/mL, 1 mM NaCl, pH 9.0 solution with a heating and cooling temperature program. *Time = 0 – 7 hrs:* the polymer-free fluid undergoes heating and cooling from 25 – 45°C and back at 5 °C increments. *Time = 7 – 7.5 hrs:* adsorption of star polymers at 25°C. *Time = 7.5 – 17 hrs:* heating and cooling of the adsorbed layer with star polymer remaining in the bulk solution. The cloud point of the PDMAEMA(62) stars is ~35 - 40 °C at pH 9.0. Most notable are the substantial frequency shifts observed at 40 – 45 °C. Values for the frequency and dissipation shifts upon initial adsorption (Δf_1 and ΔD_1) and after temperature processing (Δf_2 and ΔD_2) are displayed to highlight thermally-induced hysteresis resulting in excess adsorption.

Similar temperature-induced hysteretic effects are observed for

PDMAEMA homopolymer stars on silica as displayed in **Figure 8.9**. QCM-D

with a temperature program is utilized to assess the room temperature adsorption and subsequent effects of heating and cooling above the cloud point. Initial adsorption of star PDMAEMA at 25°C and pH 9.0 results in Δf_1 and ΔD_1 of -19 Hz and 1.6×10^{-6} . The adsorbed layer is then heated and cooled at 5°C increments without rinsing the polymer from the bulk solution. The cloud point of PDMAEMA homopolymer stars at pH 9.0 was measured immediately prior to the experiment to be approximately 37 °C. This temperature response is evident in QCM-D upon heating to and above the cloud point. An extremely large change in the frequency shift is measured upon heating from 35 – 40 °C, indicating that the thermal transition temperature has been reached. Further changes in the frequency shift occur upon heating to 45 °C, reaching values of ~ -625 Hz. The opposite trend occurs when cooling the system below the cloud point, however the process is not fully reversible. After returning to 25 °C, the adsorbed layer does not return to the values Δf_1 and ΔD_1 observed for the initial adsorption prior to heating. Instead the measured frequency and dissipation shifts, relative to the the bare crystal before any adsorption occurred, are Δf_2 and ΔD_2 are -116 Hz and 13.5×10^{-6} . The significantly larger frequency and dissipation shifts after thermal processing indicates that additional star PDMAEMA has been incorporated on the surface. At temperatures above the cloud point, the bulk solution undergoes aggregation and likely nucleates a microphase transition on the surface¹⁶. The adsorbed layer also bears a different microstructure than the simple, sub-monolayer conformation assumed after initial adsorption. A dissipation shift of 13.5×10^{-6} suggests a significantly more extended layer conformation with

different mechanical and shear properties. The order of magnitude increase in the frequency shift corresponds to an order of magnitude increase in Sauerbrey mass.

8.3.3 *Normal and frictional forces measured by colloidal probe AFM*

This section will investigate the surface forces resulting from the adsorbed star polymers layers discussed above. The normal force profiles upon adsorption of the star polymers will be assessed in an effort to identify the nature of the interaction forces between adsorbed stars. These forces can be electrostatic, polymer-mediated steric repulsions, attractive polymer-polymer interactions, polymer-surface bridging forces, van der Waals interactions, or hydrophobic effects. The interplay between these different interactions will determine the adhesive or repulsive force profiles measured upon approach and retraction of the star polymer coated surfaces and additionally influence the frictional sliding characteristics. Ultimately, the friction characteristics resulting from the adsorbed layers will be evaluated based on the coefficient of friction and zero-load friction force measured by colloidal probe method:

$$F_f = \mu F_n + F_{f,0} \quad (8.3)$$

This method of analysis allows for comparisons of the layers based on their lubricity (friction coefficient, μ) and the relative strength of their adhesive interactions ($F_{f,0}$).

Particular attention will be paid to the pH-induced swelling behavior of the layers that was observed in the previous section. The layer thickness, charge, and degree of hydration are all important factors contributing to the performance

of the star polymers as friction control lubrication layers. The ability of pH to trigger conformational changes in the adsorbed stars will be identified by normal force measurements, and correlated with the frictional sliding properties assessed via equation 8.3.

*8.3.3.1 Diblock stars, β -CD-(PMEO₂MA-*b*-PDMAEMA)*

The normal and friction force profiles between adsorbed diblock star polymers have been assessed extensively. The force and friction characteristics discussed here in **Figure 8.10** and **Figure 8.11** follow the same experimental procedure as the QCM-D experiment in **Figure 8.6**. This sequence involves: 1) examining the effect of polymer concentration on the extent of adsorption at pH 9.0, effectively spanning the adsorption isotherm from the low-coverage to saturation regimes; 2) rinsing the layer to pH 5.0 to swell and charge the PDMAEMA blocks; 3) rinsing the layer back to pH 9.0 and exposing to higher salt concentration and salt-free rinses. Following the exact same sequence in QCM-D and AFM experiments allows for direct linkages to be made between the adsorbed layer properties and conformation and the measured interaction forces. Pre- and post-friction force curves are shown to highlight wear effects or shear-induced changes in layer properties.

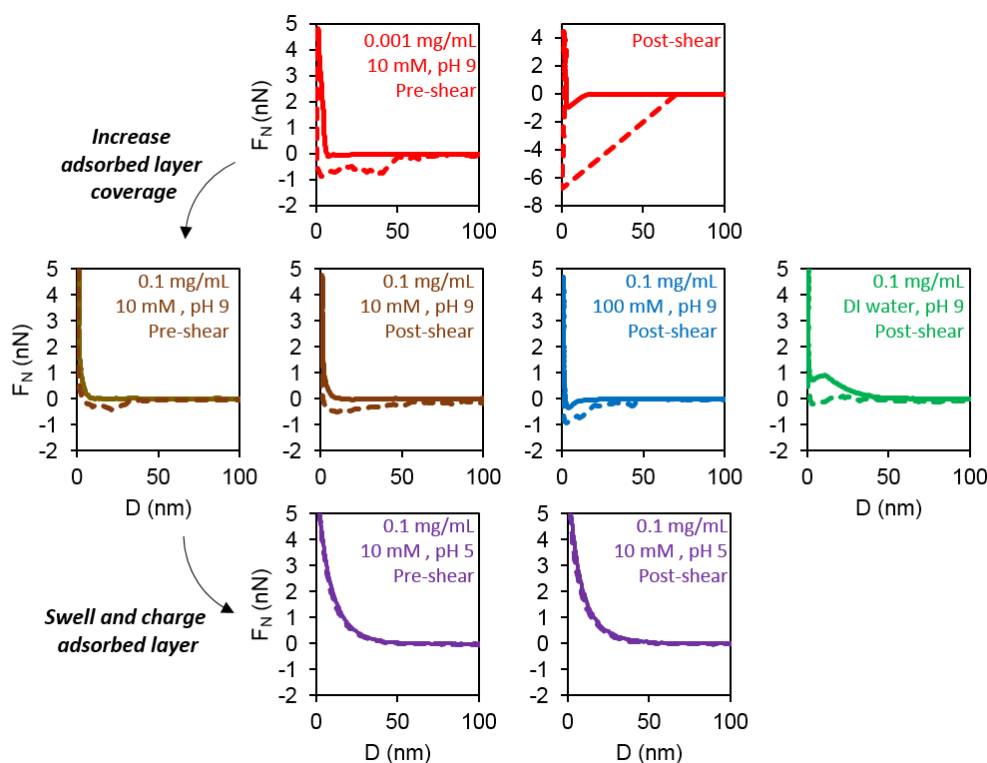


Figure 8.10. Normal force versus distance profiles between a 20 μm diameter silica colloidal probe and flat silica surface each bearing adsorbed 14-arm, diblock PMEO₂MA-*b*-PDMAEMA star polymers. Solid lines are the forces on approach and dashed lines are the forces on retraction of the surfaces. Panels are labeled with solution conditions (polymer bulk concentration, NaCl concentration, pH) and whether or not the force profile is obtained before or after the friction measurements (shown below in Figure 8.11). The rows can be categorized from top to bottom as “strongly adhesive”, “weakly adhesive”, and “purely repulsive”, which correlate with three observed frictional regimes.

Initial adsorption of the diblock stars occurs at 0.001 mg/mL, and the normal force curves (Figure 8.10) display repulsions on approach and adhesion on retraction, consistent with a low-coverage adsorbed layer and polymer-surface bridging. The measured force curves after friction now display attractive forces on approach and significantly stronger adhesion on retraction of the probe. Both these features suggest that the adsorbed layer has been damaged by the

compression and shear. This is consistent with the picture of a low-coverage adsorbed layer and strong bridging-adhesion. Adsorption of diblock copolymer stars at a higher bulk concentration of 0.1 mg/mL returns the approach curves to being purely repulsive, confirming that the layer has been “healed” by fresh adsorption of stars. The retraction force curves still exhibit adhesion, and this is likely a combination of polymer-surface bridging and segment-segment attractions from the weakly solvated MEO₂MA blocks. However, the adsorbed layer displays little damage after compression and shear, indicating that the layer has a sufficient thickness and binding strength to support sliding. Finally, the layer is swollen and charged by rinsing to pH 5.0. The force curves switch to fully repulsive behavior and exhibit no adhesion on approach, retraction, or after shearing. This is consistent with the strong swelling and hydration of the layer as observed in QCM-D. The electrosteric repulsions imparted by the charged PDMAEMA are sufficient to swell the layers prevent bridging and/or any attractive PEO₂MA segment-segment attractions observed previously at pH 9.0. Further force curves are obtained after rinsing back to pH 9.0 and subsequently changing the salt concentration. The force curves at both 100 mM NaCl and in salt-free DI water (adjusted by NaOH to pH 9) continue to display similar adhesions as were observed at pH 9.0 in 10 mM NaCl, suggesting that the adhesive interactions are not particularly sensitive to the ionic strength environment. The approach curves for 100 mM NaCl and DI water display different features – 100 mM NaCl yields only attractions on approach and DI water shows a primary repulsion followed by a secondary, attractive force. This

can be attributed to the effective electrostatic interactions between the layers that arise from the negatively charged surface being coated with a neutrally charged polymer. The long-range repulsions observed in DI water for the star polymer layers display a decay length of ~ 50 nm, consistent with the measured Debye length for salt-free silica-silica repulsions at pH 9 (See Section 2). This is larger than the effective layer thickness, thus the repulsions dominate at larger separations and give way to bridging as the surfaces are brought to separations on the order of the layer thickness. The electrostatic repulsions are screened in 100 mM, thus only bridging is observed. Overall, the diblock stars display remarkably versatile normal interaction forces. The interactions on approach can be tuned from weakly repulsive to purely attractive to strongly repulsive, which is important for lower-load applications. Under strong compression the surfaces will be driven into close contact and into the deep adhesive well. Here, we can modulate the strength of the adhesive forces from weakly adhesive to strongly adhesive to purely repulsive.

The friction properties of the diblock star polymer adsorbed layers discussed above are shown in **Figure 8.11**. Here the raw AFM lateral deflection and normal deflections are shown in units of photodiode voltage change. These values are directly proportional to the friction and normal forces between the layers. The measurements are obtained with the same cantilever, probe, and optical alignment, and thus the forces can truly be compared without concern for error from slight misalignments in the probe position or laser spot that can occur

when comparing separate independent measurements. The linear fits for the coefficient of friction based on raw voltage data are not the true coefficients of friction defined with respect to forces, which are tabulated below in **Table 8.2**. However, the relative changes in slope shown on the figure are equivalent to relative changes in the coefficient of friction.

Three regimes emerge in the friction versus load curves for the diblock stars in Figure 8.11, and each regime can be associated with characteristic features of the corresponding normal force versus distance profiles in Figure 8.10. First is the adhesion-controlled regime observed for the low-coverage adsorbed layer at pH 9.0, labeled as “strongly adhesive” in the figure. The large y-intercept, or zero applied load friction force, correlates with the strong adhesion measured on retraction of the surfaces. Here, bridging contacts dominate and little to no polymer-polymer repulsion is present to prevent bridging of the surfaces. It is notable the friction slightly deviates from Amontonian behavior. This non-linear behavior is expected for adhesion-dominated friction and can be explained in terms of the non-linear JKR evolution of the contact area^{17,18}. In the second regime, labeled “weakly adhesive”, adsorbed layers display much lower zero-load friction forces than in the adhesion-controlled regime. These layers all exhibit weak adhesion in normal force profiles on retraction of the surfaces, and do not undergo shear-induced damage (force curves same before and after compression and shear) owing to the increased coverage of polymer on the surface at a higher bulk polymer concentration. Both 100 mM and salt-free conditions exhibit similar friction coefficients and zero-load friction forces owing to the strong applied

loads that force the layers into the same adhesive bridging interactions that are measured on retraction. Finally, a third regime labeled as “purely repulsive” that displays consistently low friction compared to the other cases is observed for the swollen, charged layer after rinsing to pH 5.0. Recall, this is the layer that displayed purely repulsive normal forces and no bridging. Not only is there no zero applied load friction, the coefficient of friction for the swollen layer at pH 5 is approximately 20 – 30 times lower than the coefficient of friction of the weakly adhesive layers at pH 9.0. This is another example of pH-induced friction control, and for the PEO₂MA-*b*-PDMAEMA diblock star it occurs via swelling and charging of the PDMAEMA blocks in the diblock star adsorbed layer. Also, the friction coefficient is approximately 50% higher in 100 mM NaCl than is measured for the same adsorbed layer in 10 mM NaCl. This is likely attributable to the further screening of segment-segment repulsions that increases frictional losses from interpenetration inside the compressed brush layer. Ultimately, the versatile range of friction and adhesion properties observed here between adsorbed diblock star polymers makes them attractive for friction control applications. Temperature effects on the surface forces have not been investigated.

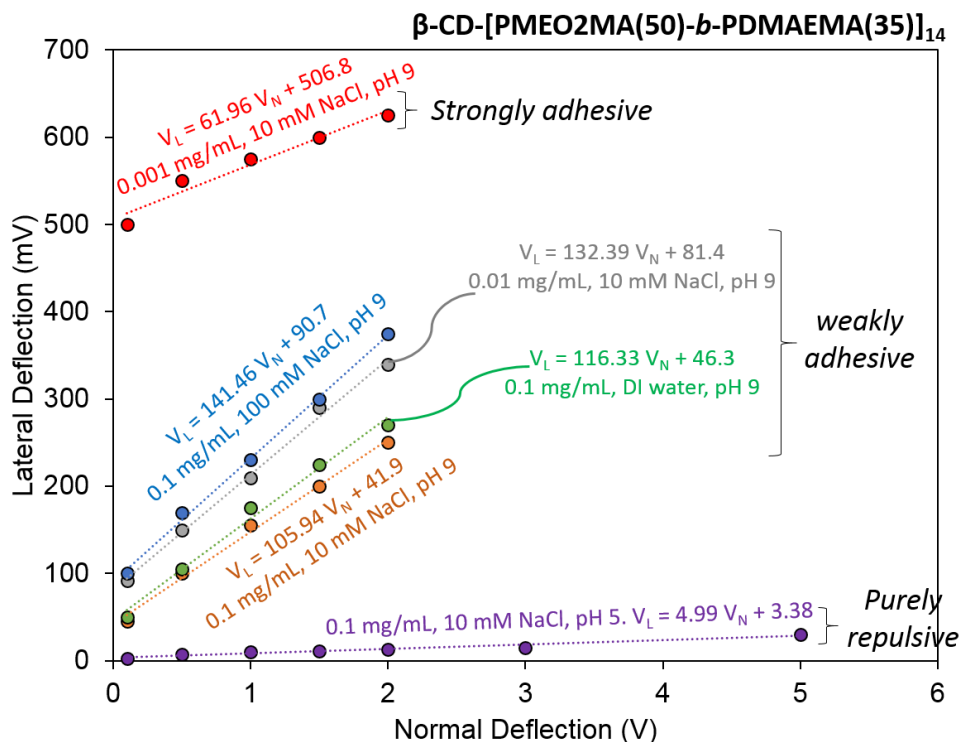


Figure 8.11. Friction forces between a 20 μm diameter silica colloidal probe and flat silica surface each bearing adsorbed 14-arm, diblock PMEO₂MA-*b*-PDMAEMA star polymers. Raw AFM deflection signals, lateral and normal, are shown because the same cantilever and laser setup were used for all measurements. Lateral deflection is proportional to friction force and normal deflection is proportional to applied load. Solution conditions (polymer bulk concentration, NaCl concentration, pH) and linear fits are labeled for each curve. Three identifiable regimes correlate with the adhesive properties of the normal force profiles measured on the same adsorbed layers (see Figure 8.10). Note: the raw coefficient of friction displayed here has units of lateral mV per normal V. A conversion is required to convert to the true, dimensionless COF tabulated in Table 8.2.

8.3.3.2 Triblock stars, β -CD-(PMEO₂MA-*b*-PDMAEMA-*b*-PMPC)

Surface forces have also been measured between adsorbed triblock star layers. The assessment of interactions between triblock stars is less extensive than presented above for the diblock stars, but interesting features have still been observed and preliminary interpretations of the data are given. The normal force

profiles for adsorbed triblock stars are given in **Figure 8.12**. The normal force interactions are again measured initially at pH 9.0 in 10 mM NaCl then subjected to rinses to pH 5, 10 mM NaCl rinses to investigate the effect of PDMAEMA charge on the interactions. The force curves are obtained here in the same sequence as the QCM-D measurement in **Figure 8.7**, so statements about the behavior of the adsorbed layer are made on the basis of an independent measure of the layer thickness and swelling.

After initial adsorption at pH 9.0, the triblock stars display purely repulsive forces on approach and retraction. This is consistent with the relatively large Voigt mass measured in QCM-D. Interestingly, the layer exhibits no adhesion at pH 9.0, which is in contrast to its precursory PMEO₂MA-b-PDMAEMA diblock star that exhibited bridging under the same conditions. This suggests that the presence of a peripheral zwitterionic block imparts an additional steric interaction force on the stars. This is also consistent with the thermal aggregation studies previously shown in **Figure 8.5**. The triblock stars showed no significant large-scale aggregation upon modest heating where the diblock stars formed large scattering entities and flocs. The force measurements are not fully analogous with the temperature-driven aggregation studies, but the adsorbed star polymer layers do undergo a significant compression and confinement in the colloidal probe measurements, achieving an effectively large polymer volume fraction in the confining region. The ability of the triblock stars to maintain adsorbed layer repulsions under high volume fraction conditions indicates that the

zwitterionic blocks at least prevent attractive EO₂MA segment-segment contacts from occurring.

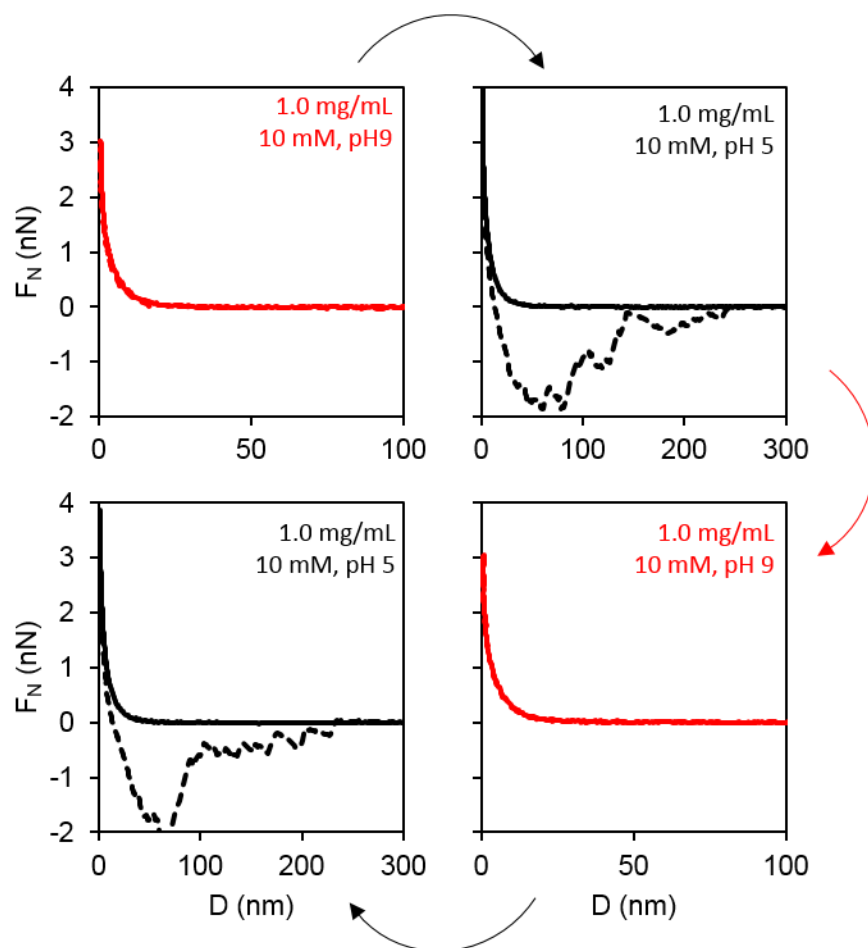


Figure 8.12. Normal force versus distance profiles between a 20 μm diameter silica colloidal probe and flat silica surface each bearing adsorbed 14-arm, triblock PMEO₂MA-*b*-PDMAEMA-*b*-PMPC star polymers. Panels are labeled with solution conditions (polymer bulk concentration, NaCl concentration, pH). Rinses with polymer in solution occur to change the solution pH from pH 9.0 to pH 5.0 over two cycles.

Interestingly, adhesion occurs between the triblock star adsorbed layers upon rinsing to pH 5.0. This effect is opposite from what was observed for the diblock star, where rinsing to pH 5.0 cause the diblock layer to swell and transition from adhesive to repulsive behavior. It is unclear what causes this effect

in the case of the triblock stars, but the adhesion traces upon retraction display multiple pull off events that are characteristic of bridged polymer segments. It is possible that the triblock star assumes a different initial adsorbed layer conformation at pH 9.0 than the diblock star, causing the resulting rinse to pH 5.0 to have a different effect on the interactions. For example, it is possible that the zwitterionic group shields the PDMAEMA and PMEO₂MA segments from bridging at pH 9 when the inner two blocks are both relatively collapsed. Upon rinsing to pH 5.0 the PDMAEMA block is charged and assumes a more extended conformation away from the inner PMEO₂MA block and enables bridging across the gap. This phenomenon needs to be investigated further, but the observations indicate yet another level of control over interaction forces. If one desires adhesive behavior at lower pH, then the triblock star with the zwitterionic outer block is the appropriate material, whereas the diblock star with the outer PDMAEMA block is the appropriate material if one desires non-adhesive interactions at lower pH.

The friction characteristics of the adsorbed triblock polymers are presented in **Figure 8.13**. The friction properties for the purely repulsive triblock star adsorbed layer at pH 9.0 exhibits a relatively low coefficient of friction. The layer also displays a zero-load friction force that is not positive, consistent with no adhesion. Unique friction versus load behavior is observed for the triblock star upon rinsing to pH 5.0. The force curves indicate that the layer is moderately adhesive here, and the layer in fact presents a zero-load friction force that is consistent with the adhesion measured in the normal force profiles. However, the friction force is

strongly non-linear with respect to increases in the applied load. There appears to be a transition from low coefficient of friction behavior to a higher coefficient of friction somewhere between 2 – 3 V of applied load (11 – 17 nN, force). This indicates that the dominant lubrication mechanism changes in response to the increased confinement of the layers. It is possible that the low coefficient of friction sliding is initially supported by the strongly hydrated, zwitterionic blocks, and on further compression of the layers the lubricity is no longer maintained. It is possibly due to forced bridging interactions or forced interaction of MEO₂MA segments, but the mechanism is not clear. The friction characteristics of the adsorbed triblock star polymer layers merit further investigation.

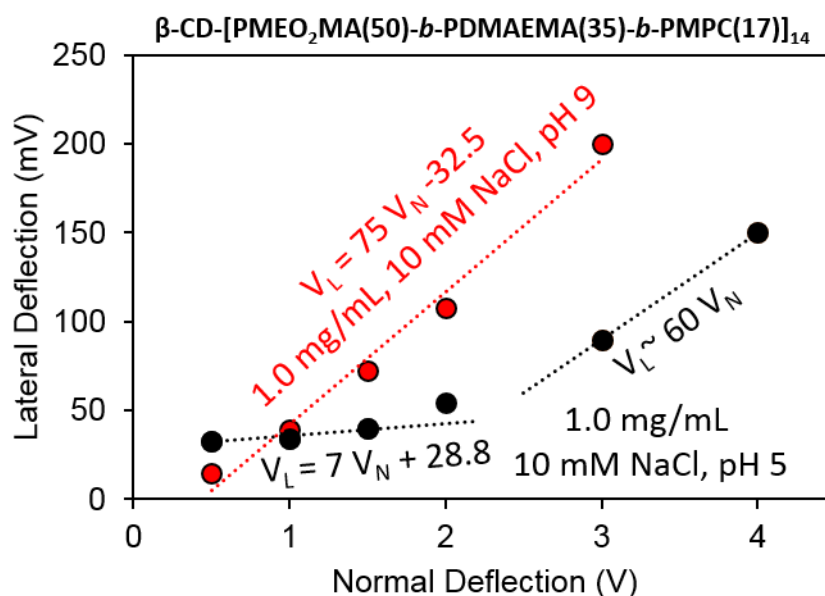


Figure 8.13. Friction forces between a 20 μm diameter silica colloidal probe and flat silica surface each bearing adsorbed 14-arm, triblock PMEO₂MA-*b*-PDMAEMA-*b*-PMPC star polymers. Raw AFM deflection signals, lateral and normal, are shown because the same cantilever and laser setup were used for all measurements. Note: same cantilever and probe type as used in other friction measurements this chapter. Solution conditions (polymer bulk concentration, NaCl concentration, pH) and linear fits are labeled for each curve, including two apparent friction regimes at pH 5.

8.3.4 *Comparison of friction coefficient for 14-arm stars*

A summary of the coefficient of friction and zero-load friction forces fit from friction versus load data is presented in Table 8.2. This table is not comprehensive, rather it provides a comparison between the frictional properties of adsorbed star polymer layers under conditions where bulk polymer concentrations, salt concentration, and pH values are constant. This is an attempt to isolate the effects of the adsorbed polymer layer structure, although it still remains difficult owing to subtle differences in the adsorbed layer conformations. The table is meant to provide a coarse summary of the frictional properties and their response to changes in solution pH between 5 and 9. The coefficients of friction are meant for comparisons of the lubricity of the layers, while the zero-load friction force is a measure of the adhesiveness of the layer. We observe low coefficients of frictions for each star polymer adsorbed layer. The lowest coefficients of friction appear at pH 5, where the cationic blocks are ionized, and values between 0.04 – 0.10 are measured. The coefficients of friction summarily increase upon rinsing to pH 9, reaching 0.35 – 1.05. The pH-driven transition between ionization states provides a convenient route to modify friction between surfaces, and low coefficients of friction in the ionized state suggest that the various polymers have potential as aqueous boundary lubricants. However, the triblock star polymers did not exhibit any particularly enhanced lubrication properties relative to the diblocks. Very low friction has been observed for dense, high grafting density PMPC brushes¹⁹ and adsorbed PMPC bottle brush polymers¹³, but may not be realizable in star polymer layers.

Table 8.2. Amontonian friction with adhesion fits for star polymer layers

Solution Conditions	Coefficient of Friction, μ	Fit Zero-Load Friction (nN)	Max Applied Load (nN)	Misc. Notes
Homopolymer PDMAEMA Star				
pH 5	0.101	0.5	13.5	pH 9 bridging prevented at 0.01 mg/mL polymer conc.
pH 9	0.354	0.1	13.5	
Diblock star				
pH 5	0.039	0.2	11.0	Shear damage prevented @ 0.01 mg/mL polymer conc. [NaCl]↑, μ ↑
pH 9	1.054	3.8	27.5	
Triblock star				
pH 5	0.059	1.3	22.0	Reversible μ switching between pH 5 and pH 9
	0.512	-4.2		
pH 9	0.637	-1.5	16.5	

8.4 Conclusions

We synthesized a series of water-soluble, stimuli-responsive 14-arm star polymers via atom-transfer radical polymerization from initiator functionalized cyclodextrin cores. The star polymers included homopolymer stars and stars with di- or tri-block arms. Weak cationic PDMAEMA imparted pH- and temperature responsive properties to the stars and this was utilized to both swell/deswell the stars and also direct electrostatic adsorption of the stars to negatively charged silica surfaces. PMEO₂MA imparted a pH-independent temperature response close to but above room temperature that, when paired with the pH-dependent

temperature response of PDMAEMA, lead diblock PMEO₂MA-*b*-PDMAEMA stars to manifest dual-transition aggregation behavior in response to heating. Triblock star polymers were prepared by attaching a short zwitterionic PMPC block to the end of the PMEO₂MA-*b*-PDMAEMA diblock star polymer arms. The peripheral zwitterionic group provides a sufficient steric barrier that enables triblock star polymer to resist thermally-induced aggregation that the diblock stars were susceptible to. We propose that the triblock star consists of a globular, collapsed core of PMEO₂MA with the hydrophilic PDMAEMA and PMPC blocks extending away in a star conformation. The triblock stars are being studied further to better understand the structure and properties with respect to orthogonal temperature and pH effects.

The adsorption and surface forces between adsorbed star polymer layers were measured in an effort to assess the star polymers as agents for large dynamic friction control. PDMAEMA-containing homopolymer, diblock, and triblock stars all adsorbed readily to silica surfaces and imparted interesting polymer-mediated and pH-responsive interactions. Diblock stars displayed strikingly versatile normal and friction force characteristics, all of which were tunable by changes in pH or ionic strength. Triblock stars displayed uncharacteristic interactions that at the time of this dissertation are tentatively ascribed to load-induced restructuring of the layers. The star polymer layers all produced low to modest friction coefficients that would rationalize their use as boundary lubricants or stimuli-responsive thin film coatings.

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9. Conclusions, perspectives, and future work

9.1 Summary of adsorption strategies used to control normal and frictional forces between polymer brush nanoparticle-coated surfaces

This dissertation utilized a number of materials, adsorption conditions, and processing schemes to produce brush nanoparticle adsorbed layers with engineered structure and interaction forces. The following schematics are intended to provide a summary of the major findings that are unique to polymer brush nanoparticle adsorption and surface forces.

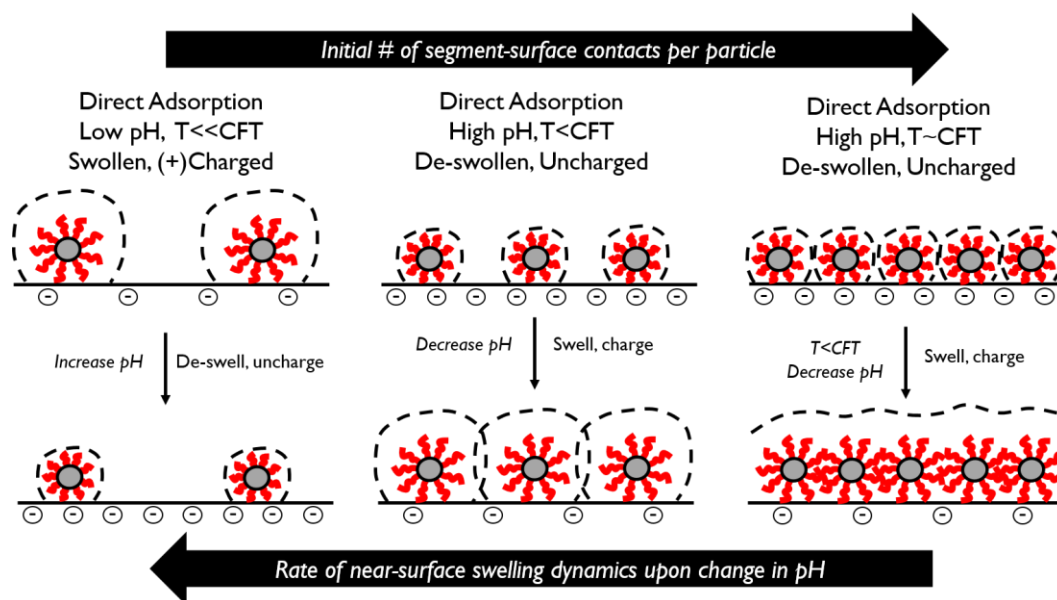


Figure 9.1. Summary of pH- and temperature-effects on the adsorption of PDMAEMA grafted silica nanoparticles. The number of adsorbed particles can be increased by tuning electrostatic interactions *via* pH or solvent quality *via* temperature. Adsorbed particles can ionize and swell in response to changes in pH, and it is hypothesized that the near surface structure of the adsorbed layers controls the hysteretic adsorption characteristics. Conformational changes are kinetically limited owing to the large number of polymer segments in contact with the surface, therefore slowing down dynamic effects in the vicinity of the surface.

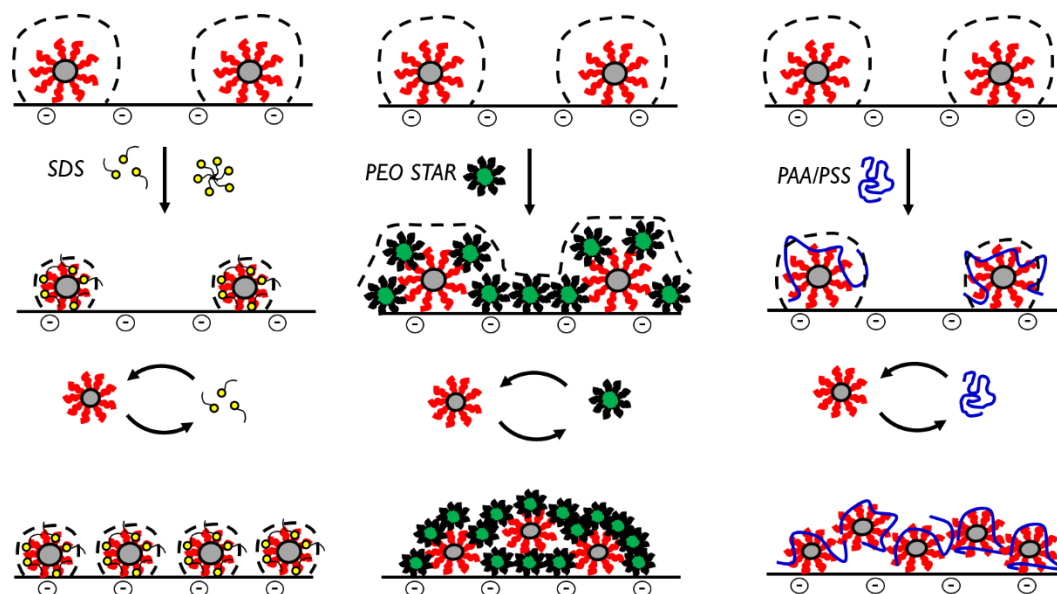
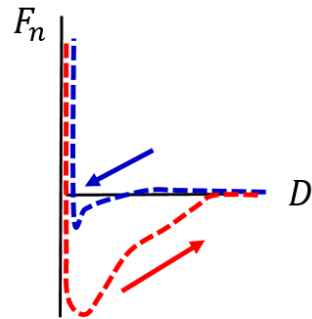
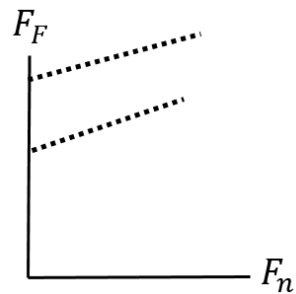
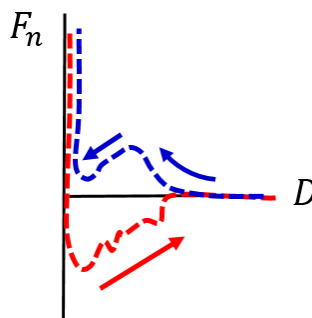
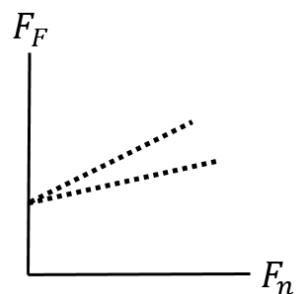
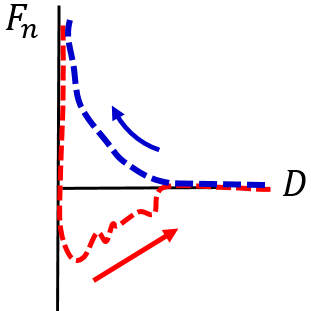
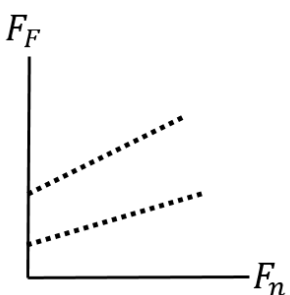
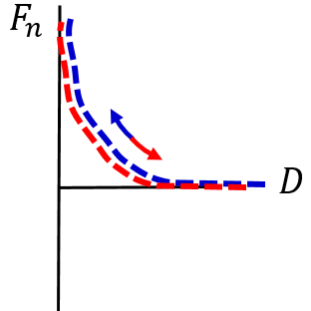
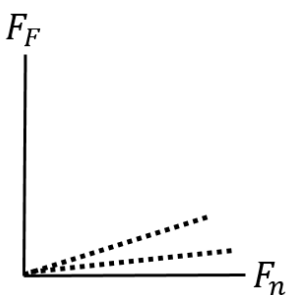


Figure 9.2. Summary of sequential adsorption strategies to form engineered, multi-component adsorbed layers. *Left:* BNPs with oppositely charged surfactant. Surfactant binding collapses the brush and reduces the effective charge repulsion of particles on the surface, enhancing the overall number density of BNPs on each surfactant/BNP adsorption cycle. *Middle:* BNPs with non-ionic star polymer. BNP layers whose coverage is limited by lateral repulsions will manifest bridging adhesion due to exposed substrate. Non-ionic star polymers can backfill the gaps between BNPs with a dense-brush like layer. Multi-layers can be formed by sequential adsorption to assemble thick, mixed brush layers. *Right:* BNPs with oppositely charged linear polyelectrolytes. Traditional layer-by-layer adsorption can assemble thicker films due to charge overcompensation on each adsorption step.

Table 9.1 Generalized normal force and friction regimes identified for adsorbed BNP layers.

Regime	Normal Force Profiles	Friction versus Load	BNP Layers	Responsive properties
I. Pure bridging attraction			Bare probe versus adsorbed layer on surface. Layers with weak electrostatic repulsions and strong polymer-polymer attractions.	Range and strength of bridging attraction. Tunable to (II).
II. Electrostatically hindered bridging			Asymmetric probe/surface coverages. Patchy layers with long-range surface-surface electrostatic repulsions	Strength and range of primary electrostatic repulsions. Coefficient of friction Tunable to (I)

III. Repulsive under weak confinement			Asymmetric probe/surface coverage. Intermediate coverage, patchy BNP layers.	Strength and range of repulsions and bridging adhesion. Coefficient of friction. Tunable to (IV)
IV. Repulsive under strong confinement			High coverage layers.	Range and strength of repulsions. Coefficient of friction. Tunable to (III)

9.2 Conclusions

Polymer brush nanoparticles with well-defined molecular structure have been synthesized via atom-transfer radical polymerization. The dissertation focused primarily on the assessment of three types of polymer brush nanoparticles: multi-arm non-ionic core-crosslinked star polymers, silica nanoparticles grafted with a weakly cationic polyelectrolyte brush, and 14-arm block star co-polymers. The polymer brush nanoparticles were designed with components that allow the particles to adsorb at the solid/liquid interface.

Non-ionic core-crosslinked PEO star polymers had a hydrodynamic diameter of approximately 25 nm in aqueous solution. They adsorbed readily to silica surfaces through hydrogen bonding interactions and formed densely-packed, brush-like layers in the pH range 5 – 8.5. At higher pH, star PEO adsorption to silica is limited by a reduced population of surface silanol groups. Interactions between surface-saturated star PEO layers were purely steric repulsions, and modestly low coefficients of friction were attained. The competitive adsorption of star PEO and linear PEO was found to be strongly dependent on the molecular weight of the linear polymer.

SiO₂-*g*-PDMAEMA displayed pH and ionic strength dependent size and charge properties. They adsorbed readily to silica surfaces through electrostatic interactions, and surface coverage involved a delicate balance between lateral particle-particle electrostatic repulsions and particle-surface attractions. A sharp adsorption maximum with respect to pH is observed near the SiO₂-*g*-PDMAEMA isoelectric point, providing a narrow window of conditions for dense particle

packing. SiO₂-*g*-PDMAEMA also flocculates upon heating owing to the lower-critical solution temperature of PDMAEMA. Temperature can be used in tandem with pH to reduce the solvent quality of water and achieve the densest packing of particles on the surface. SiO₂-*g*-PDMAEMA adsorption is strongly hysteretic, and we attribute this to the hindered dynamics after initial adsorption and formation of multi-segment contact with the surface. Thus, SiO₂-*g*-PDMAEMA can be swollen and de-swollen by modulating solution pH in a repeatable fashion without significant particle detachment. pH processing strategies can effectively tune the surface coverage and bridging interaction, providing a route for responsive force and friction behavior. At an appropriate surface coverage, strong adhesion and high friction can be switched to pure repulsions and low friction simply by swelling and charging particle layers using particle-free pH rinses.

Multi-component mixed adsorbed layers were also studied in efforts to produce high-coverage BNP adsorbed layers. Sequential adsorption was used to study surfactant binding to SiO₂-*g*-PDMAEMA, mixed SiO₂-*g*-PDMAEMA/star PEO multilayers, and layer-by-layer assembly of BNPs and linear polyelectrolytes. Each method proved useful for pushing the coverage and thickness of adsorbed layers past the limitations achievable for individual, sub-monolayer BNP assemblies.

A final study investigated novel 14-arm star polymers with rationally designed block-copolymer arms grafted from cyclodextrin cores. A series of structurally related star polymers were synthesized, ultimately resulting in non-ionic, cationic, and zwitterionic homopolymer stars, a non-ionic/cationic diblock

star, and a non-ionic/cationic/zwitterionic triblock star. The thermal aggregation, adsorption, and force and friction properties of the layers were preliminarily evaluated. The diblock stars exhibited double-transition thermal aggregation and fully-switchable pH-induced adhesion and friction properties. The triblock star exhibited enhanced thermal aggregation stability from the addition of peripheral zwitterionic blocks, and resulted in low-friction behavior similar to that of the diblock stars.

9.3 Original Contributions

The research findings in this dissertation provide a number of contributions across the broad fields of polymer adsorption, colloidal and surface forces, and polymeric nanomaterials. The assessment of polymer brush nanoparticle adsorption at the solid/liquid interface in this dissertation complements the previous work performed in our group that studied polymer brush nanoparticles at the fluid/fluid interface for high-efficiency emulsification. In tandem with the dissertation of T. Saigal (“Development of Novel Pickering Emulsifiers using Polymer Grafted Nanoparticles”), the surface activity and interfacial properties of core-crosslinked PEO star polymers and PDMAEMA-grafted silica nanoparticles have been measured over a broad range of pH, temperature, and processing conditions. Together, these works have established polymer brush nanoparticles as a novel class of functional surfactant materials.

The emphasis placed on friction control and tunable bridging interactions in this dissertation mark a significant departure from the prevailing tendency in the current literature to focus on designing polymeric materials and brush-like layers

that merely reduce friction or attain a low coefficient of friction. We have been able to achieve a dynamic range of friction coefficients over 3 orders of magnitude by changing adsorption and surface coverage conditions. Additionally, the broad range of adhesive interactions encountered for the PDMAEMA-grafted silica BNP adsorbed layers and block-arm star polymers as a function of surface coverage and swelling state is relatively unprecedented in the current literature. The ability to engineer layers that are repulsive under weak confinement (*ex.*, sheared colloidal suspensions bearing adsorbed BNPs) but adhesive under strong confinement (*ex.*, boundary lubrication), and the strength of both these forces being tunable via pH or temperature, highlights the robust behavior of BNPs and the broad applicability for which they can provide beneficial technological enhancements.

9.4 List of some unanswered questions

Chapter 3

- How is preferential adsorption and displacement of star PEO by linear PEO influenced by enthalpic interactions? Which structure adsorbs prevalently under weak adsorption conditions?
- How can changing solvent quality via the Hofmeister series be evaluated for adsorption to a solid/liquid interface? Can a different substrate other than silica be used to isolate solvent quality effects without strong changes in surface chemistry on exposure to the broad pH range exhibited for different Hofmeister salt types and concentrations?

Chapter 4

- How do BNPs adsorb to other types of substrates, such as hydrophobic surfaces?
- What is the electrical potential landscape near the surface for patchy, brush nanoparticle-coated silica surfaces? Is an effective potential established across the surface, or does charge remain discretely segregated in negatively and positively charged patches?
- What is the true origin of the strong adsorption hysteresis effect for PDMAEMA grafted nanoparticles on silica surfaces? Can these dynamics be modified by changing the polymer-surface interactions?

Chapter 5

- Can separate electrostatic and steric interactions be identified from colloidal probe measurements of BNP interactions?
- How does interdigitation of particles contribute to the measured friction forces, as distinct from polymer chain interpenetration? Can patterned layers of BNPs or layers exhibiting long-range order be used to better understand interdigitation?
- How do microscopic friction trends hold up in macroscopic tribology measurements? What do the Stribeck curves look like? Can suspended BNPs contribute to hydrodynamic lubrication and provide mixed lubrication benefits?

Chapter 6

- How do the nanomechanical properties of brushes change upon SDS-induced brush collapse? Is this collapse a first-order or continuous phase transition?
- Can a surfactant mesophase form between closely packed BNPs upon exposure to surfactant concentrations above the critical micelle concentration? What forces arise between these 2D microstructures?

Chapter 7

- How does star PEO interact and bind with PDMAEMA BGNPs?
- What are the mechanical properties of thicker multilayer films with incorporated BNPs? Do BNPs act like strong crosslinkers and increase the effective film modulus?

Chapter 8

- What is the conformation of the block stars in solution? Are the diblock and triblock core-shell? How does the presence of well-solvated peripheral PDMAEMA and PMPC blocks influence the inner, poorly solvated PMEO₂MA blocks? Can contrast matched small angle neutron scattering be used to elucidate these effects?
- What kind of self-assembled structures form upon heating? Do micelles form? Is aggregation truly self-limiting as adsorbed for diblock stars?
- What kind of dynamic layer changes occur during compression of block star polymer layers? Can the spatial ordering or length of blocks be used to design layers with well-defined dynamic adsorbed layer transitions?

9.5 Future work

9.5.1 *Friction-mediated shear-thickening suspension rheology*

Recent research has found that frictional interactions play an important role in the emergence of shear-thickening rheological behavior in dense colloidal suspensions^{1,2}. The recent simulations incorporated frictional contacts in addition to hydrodynamic interactions, and succeeded in predicting strong discontinuous shear thickening effects in dense suspensions of both Brownian and non-Brownian particles. Shear thickening emerges in the simulations of dense suspensions upon incorporating a non-zero coefficient of friction, and the change in viscosity upon shear thickening increased with increasing coefficient of friction. The result suggests that shear thickening rheology is realizable without any significant change in suspension microstructure such as particle aggregation. Experimental validation of this mechanism requires a method to control frictional contacts between suspension particles without inducing significant microstructural association under high shear rates.

A direct extension of the work in this dissertation would involve studies of the rheological properties of BNP/colloidal silica mixtures. The force and friction characteristics measured here would provide a direct measure of frictional dissipation occurring the contact region, and the measured friction coefficient could be correlated with any observed shear thickening rheological properties. Tunable friction forces induced by BNPs could potentially be used to trigger shear thickening behavior. The surface forces measured via colloidal probe AFM

between silica surfaces is the ideal system to test the simulation predictions, which were based on suspensions of non-Brownian silica spheres.

9.5.2 *Brush-grafted nanoparticles vs brushes grafted to rough surfaces*

This dissertation identified many unique features of patchy BNP adsorbed layers and their implications for surface forces. However, BNPs are adsorbed layers possessing dynamic structure and non-permanent surface attachment. They are subject to wear and surface mobility that make identification of specific roughness effects almost impossible to correlate with friction response. An interesting follow up study would compare the friction forces between adsorbed BNP layers with those that arise between brushes that has been grown from a surface bearing rough features. One way to accomplish controlled, nano- to – micro scale roughness is to deposit colloidal silica particles onto a positively charged flat silica surface, followed by heat treatment at approximately the 1000 degrees to sinter the particles onto the wafer. Deposition of the silica particles can be controlled by salt concentration to achieve well defined rough monolayers that are permanently attached after heating. This method has been used by the Spencer research group to create roughness gradients³ on silica surfaces. In relation to this work, rough surfaces could be created using 20 nm silica nanoparticles that are approximately the same size as the nanoparticulate cores of the PDMAEMA BNPs discussed here. Growing PDMAEMA brushes from the surface with 20 nm silica rough features would mimic adsorbed BNPs at a given adsorbed coverage. This would potentially be a method to isolate roughness

effects and also identify important differences between adsorbed and grafted patchy brushes in mediating friction.

9.5.3 *Electrostatic forces between “charged” polymer brushes in non-polar media.*

This dissertation only investigated polymer brush nanoparticles in aqueous solution. This is partially due to the desire to engineer polymeric additives for aqueous-based “green lubricants” that can serve to replace traditional, volatile organic and fluoropolymer lubricants. However, many traditional lubricant formulations utilize non-polar organics oils as the base solvent or liquid medium. This is especially important in the lubrication of metallic surfaces, where aqueous lubricants can induce corrosion via undesirable electrochemical reactions at the solid/liquid interface. In addition, the higher base lubricant viscosity of liquids such as mineral oil can support stronger hydrodynamic lubrication forces than low viscosity, aqueous-based lubricants. Thus, oil-compatible brushes⁴ that assume swollen brush conformations in non-polar solvents could realize the same benefits of low-friction in boundary lubrication regime that have been studied more intensely in aqueous brush systems.

Recent advances have been made in understanding electrostatic phenomena and charge carrier formation in low-dielectric constant, non-polar media. Much of the effort in this field is focused on understanding electrostatic stabilization of dispersed colloidal particles in “doped” non-polar fluids bearing different types of surfactants and inverse micelles. Charges are stabilized within small inverse micelles in the non-polar fluid⁵ and electrostatic effects can be realized, such as

large Debye lengths. Thus, it is possible for oil-compatible brushes or brush nanoparticles to assimilate charge in non-polar fluids if the surfactant or micelles can interact, specifically or cooperatively, with chains in the brush. The complexation of charge-carrying micelles and polymer brushes may lead to apparent long-range electrostatic interaction forces across the non-polar media, and the implications for lubrication and friction are not currently under investigation in the literature.

9.6 References

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