

PREPARATION AND EVALUATION OF POLYMER COMPOSITE MULTILAYERS
ON SiO₂ FOR USE IN MEDICAL SYSTEMS

By

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Abstract of Thesis Presented to the Graduate School
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By

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Poly(diallyldimethylammonium chloride) (PDADMAC) and poly(sodium 4-styrenesulfonate) (PSS) have been consecutively adsorbed onto 1.5-μm charged silica (SiO₂) particles to model the assembling of multilayered particles for use in time released drug delivery particle systems. Time dependent adsorption studies indicate that, due to the strong ionic charge of the dissociated polycation in water, adsorption is complete in less than 30 minutes. Indications of the maximum adsorption density, changes in surface charge, and stability of the layered particles are demonstrated through adsorption isotherms and electrophoretic mobility (EPM) measurements. Further stability of the PDADMAC layer is demonstrated through multiwashing with ultra pure deionized water. Preliminary desorption studies of the PSS layer also illustrate a stabilized two-layer system.

Also, in this study, a systematic investigation on the viscosity behavior of concentrated dispersions of silica particles with adsorbed PDADMAC and PSS layers has

been performed. The variation of shear viscosity and storage and loss moduli as a function of layer number was investigated. The study illustrates that the adsorption of PDADMAC increases the viscosity. Ideal conditions for maximum bridging flocculation were also observed. From viscosity measurements of the PSS layer, a structural formation was observed at low shear rates that broke down as shear rate increased. Viscosity measurements showed that adding polymer layers to create multilayered composite particles affects the rheological properties of the particles.

Adsorbed layer thickness of PDADMAC was determined using viscosity data for dispersions of bare SiO₂ particles and dispersions of PDADMAC-coated SiO₂ particles. A comparison shows that experimental values, using relative viscosity, were comparable to values recorded in literature using different methods.

After adding SiO₂ nanoparticles (nanoSiO₂) to the mixture of PDADMAC-coated SiO₂, EPM and SEM showed a change in surface charge as well as surface roughness, indicating that the nanoSiO₂ has been adsorbed onto the layered particles. Future work includes surface and bulk property changes due to the nanoSiO₂ on the surface, as well as stabilizing this layer.

CHAPTER 1

LITERATURE REVIEW AND INTRODUCTION

Introduction to Polyelectrolyte Multilayer Research

In recent years, there has been increasing interest surrounding the fabrication of composite micro- and nano-structured materials using the self-assembly of polymers. A number of novel possibilities arise from using self-assembly processes of polymers: by involving electrostatic interactions, multilayered materials with unique and tailored properties can be built. The pioneering work on synthetic nanoscale heterostructures of organic molecules was carried out by the Kuhn group [1] in the late 1960s using the Langmuir-Blodgett (LB) technique, in which monolayers of polymer are formed on a water surface and then transferred onto a solid support as a single layer of molecular chains on the surface. Their experiments with donor and acceptor dyes in different layers of LB films provided direct proof of distance-dependent Förster energy transfer on the nanoscale. These experiments were also the first true nanomanipulations, as they allowed for the mechanical handling of individual molecular layers (such as separation and contact formation) with Ångstrom precision. However, the LB technique requires special equipment and has severe limitations with respect to substrate size and topology as well as film quality and stability.

Hong and Decher first proved the concept of alternating exposure of a charged substrate to solutions of positive or negative polyelectrolytes [2]. Provided that each adsorption step leads to charge inversion of the surface, the subsequent deposition finally results in a layered complex, stabilized by strong electrostatic forces, so-called self-

assembled polyelectrolyte multilayers. Since the electrostatic interactions are a very general principle, the process is very versatile with respect to the incorporation of different charged compounds or nanoobjects. As building blocks, for example, inorganic nanoparticles such as gold colloids [3], functional polymers such as temperature-sensitive compounds [4], orientable chromophores [5, 6], and mesogenic units inducing local order [7] have been employed. Further work involves the deposition of proteins into multilayers [8-12].

This principle of layer formation has not only been applied to achieve adsorption onto planar substrates but has even been applied to colloidal particles [13-16], a development which had a major impact in the field. The use of colloidal surfaces is particularly attractive, since not only can the core particle be controlled but also the particles within the layers. Micro- and nanoparticles are being studied for use in drug delivery systems [17] as well as removing toxins during water treatment [18]. Layered particles can maximize the amount of drug carried and help control diffusion rates as well as concentrations of toxins adsorbed, whether in the body or the environment. And recently, core particles that have been removed to produce hollow shell materials have promising structures for future applications [4, 19-22].

A number of external parameters, such as ionic strength of the solutions, the polyion concentration, the charge density of the polyions, and the molecular weight, are known to influence the resulting layer structure. By varying these parameters during the deposition process, there are an infinite number of structures and, thus, properties for these tailored formations.

Multilayered films of organic compounds on solid surfaces have been studied for more than 60 years because they allow fabrication of multicomposite molecular assemblies of tailored architecture [2, 23-25]. It has been well documented that the physisorption or chemisorption of polyelectrolytes onto surface-functionalized substrates can lead to the deposition of molecularly thin surface films. The controlled and selective surface modification of colloidal particles allows the fabrication of composite materials with tailored and unique properties for various applications in the areas of coating, electronics, photonics, catalysis, sensing, and separations. Composite particles that contain an inner core covered by a shell exhibit significantly different properties from those of the core itself (for example, surface chemical composition, increased stability, higher surface area, as well as different magnetic and optical properties). The surface properties are governed by the characteristics of the shell coating [26]. The interest in the fabrication of layer-by-layer assembled multicomposite particles has increased in the last few years as evidenced by the increase in the number of papers dealing with this issue.

Polyelectrolytes bearing dissociated ionic groups are one type of matter that can be used as the multilayered shell of these composite particles. Their unique properties, dominated by strong long-range electrostatic interactions, have been studied extensively over the past few decades [27, 28], and due to their ability to adsorb strongly onto oppositely charged surfaces, polyelectrolytes make good candidates for creating the multilayered shells on core particles. The concept of electrostatically driven assembly of multilayer structures allows for the incorporation of a wealth of different materials [29].

Applications for Polyelectrolyte Multilayered Particles

There is a wide application of natural and synthetic polymers in medicine, paper making, mineral separation, paint and food industries, cosmetics and pharmacy, water

treatment processes, and soil remediation [30]. A thorough understanding of polyelectrolytes has become increasingly important in biochemistry and molecular biology. The reason is that virtually all proteins, as well as DNA, are polyelectrolytes. Their interactions with each other and with the charged cell membrane are still very much a mystery.

As shown schematically in Fig. 1-1, electrostatic interactions between the polyion in solution and the surface are the key to the final structure of the polyion layered thin film; however, secondary, shorter range forces also play a role in determining the film thickness, the final morphology of the film, the surface properties, and in some cases, can determine whether or not stable multilayers can form at all.

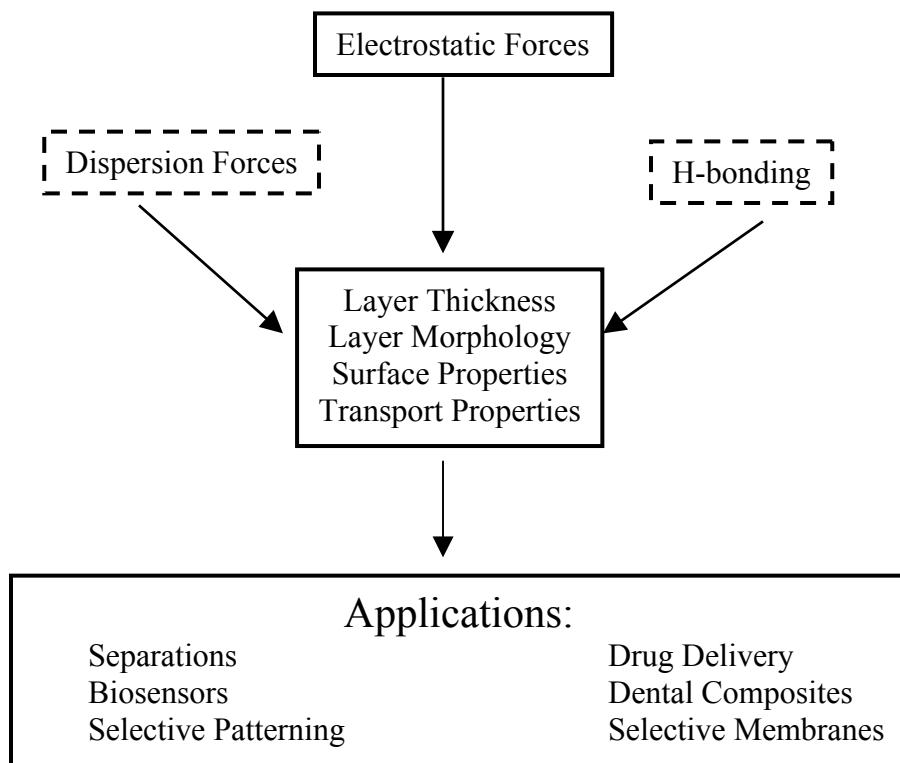


Figure 1-1: Schematic of forces influencing properties of layer-by-layer films, and the applications achieved by controlling or manipulating interactions [31].

These secondary interactions can also play a role in the selective deposition of polymers on surfaces, the formation of acentric polar structures, and the nature of permeation and ion transport within the film [31]. An understanding of these interactions, as well as an ability to combine polyions with other charged systems, dimensional polymer structures and patterns, selective membranes, and a range of functional organic and organic-organic hybrid composite thin films can be produced.

Ionic interactions are the most versatile; they permit the use of water as a solvent, which is both environmentally attractive and allows the use of charged biopolymers such as DNA, as well as polyelectrolytes, proteins, colloids, and many other charged or chargeable materials. One potential property of such devices is a simple dynamic structure in which the distance between two layers of “hard” objects (colloids or proteins) is adjusted by controlling the degree of swelling in an intermediate “soft” layer (polyelectrolyte) simply by changing, for example, humidity. The physiochemical properties of the resulting architectures can be largely modified by varying the number of deposited layers, by changing the nature of the polyelectrolytes, the pH or the ionic strength. The large versatility of the concept allows numerous applications in the biomedical field ranging from modification of biomaterial surfaces to the construction of enzymatic nanoreactors in which a cascade of reactions can be induced.

Current Characterization Techniques for Polyelectrolyte Multilayers

There are many ways to determine layer thickness as well as surface roughness. Some of the techniques that have been used are transmission electron microscopy (TEM) [21], single-particle light scattering (SPLS) [13], scanning electron microscopy (SEM) [21], atomic force microscopy (AFM) [32], nuclear magnetic resonance (NMR) [33], IR-spectroscopy, x-ray reflectivity [34], and using tagged molecules (e.g., ^{14}C).

Considerable published evidence exists [35-39] on the ability of polyelectrolytes to associate on the surface of particles, but the stability of such single or multilayer assemblies has not been thoroughly evaluated. The major advantages of layer-by-layer adsorption from solution are that multiple unique materials can be incorporated in individual layers on core particles and that the final particle architectures and properties are completely determined by the deposition sequence.

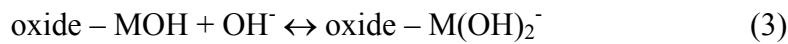
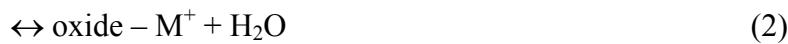
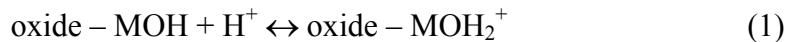
Novelty and Scope of Study

In this thesis, the basic principles of layer formation and internal properties of multilayer formation was studied, starting from simple concepts describing the initial adsorption process, and then advancing towards the bulk properties of the system, such as flow properties. The focus was on fundamental physical properties and the evolution of more realistic models from first simple model ideas for a drug delivery particulate system. Oppositely charged polyelectrolytes were used as multilayers on SiO₂ core particles. The layers of polyelectrolytes represent layers of oppositely charged species such as proteins and biological drugs. SiO₂ was used as the core because it has been used in many biomedical composites and is the main component in dental composites. If layered particles are to delivery drugs or absorb toxins from the body or the environment, a core material like SiO₂ is a practical choice. As layers of oppositely charged polyelectrolytes are sequentially adsorbed, the surface properties of the particles change—surface chemistry, charge, size—affecting bulk properties such as the conditions for flocculation and viscosity. The layers were prepared and characterized using kinetics of adsorption, adsorption studies, as well as electrophoresis and desorption studies. The mechanism of adsorption can be described as the self-assembly process involving electrostatic interactions. The internal dynamics and stability of the interacting

layers were expected to be strongly dependent on the coupling of the charges between subsequently deposited layers.

For biopolymers such as DNA and proteins, the association between counterions and the backbone chain is electrostatic in origin. In order to design new technologies with charged polymers the fundamental time scales and length scales of polymer and counterion association need to be quantified. Charged polymers present a challenge due to the long-range electrostatic interactions and coupled dynamics between small, fast-moving counterions and polymers. Practical methods such as Langmuir adsorption isotherms and electrophoretic mobility measurements were used to characterize the change of chemistry and charge on the surface. The thickness of the polymer layer which gives rise to steric stability depends on the conformation of the polymer at the interface. In order to determine the adsorbed layer thickness of the first polymer layer, conditions were kept natural with no salt or pH adjustments.

At first, polyelectrolytes were mainly used as rheology modifiers, and one of the most interesting uses of these materials has been the stabilization of a wide variety of colloidal systems. The specificity of interactions between the particles as a function of polymer layer is studied mainly through zeta potential measurements and rheological methods. In the case of inorganic oxides dispersed in water, due to the interaction of the solid colloidal particles with the dispersing phase, there is the development of charged surface sites (depending on the dispersing phase pH) according to these reactions [40]:





An ionic surface is formed and, because of these charges, ions of opposite charge tend to cluster.

During the past forty years, theories have been developed to describe the adsorption and conformation of polymer at the solid-liquid interface and also, theories have been developed to explain particle-particle interactions in the presence of polymers [16, 41-43]. Several important factors such as Brownian motion of the particles, particle size, particle size distribution, particle shape, volume fraction of the particles, the viscosity of the suspending media, and the range of particle-particle interactions govern the suspension properties.

Goal of Study

In order to tailor specific properties, a basic understanding of the structure and the control of the process of layer formation is required. There is thus a demand for further fundamental studies and for basic physical understanding. Specific properties of polyelectrolyte multilayers, which are of fundamental physical interest, include the fact that polyelectrolyte multilayers form two-dimensionally stratified layers, which grow step by step in three dimensions. This leads to a behavior being dominated by internal interfaces, and differing from the corresponding volume properties of the material.

In order to use these particles as a model for drug delivery or medical composite systems, the appropriate methods for preparation and characterization must be performed. After successfully creating multilayers of nanoscale films on SiO₂ core particles, nanoscale SiO₂ was adsorbed onto the positively charged surface.

Recently, shear thinning and shear thickening have been predicted and observed [44, 45]. Shear thickening is believed to be correlated to the loss of close packed layer ordering [46]. Addition of a polymer to a colloidal dispersion is also found to change the structural ordering dramatically and often leads to a phase separation [43, 47]. Behavior of charged colloids as a function of volume fraction (ϕ) and ionic strength has been extensively studied both experimentally [48] as well as theoretically [49]; however, the stability of colloidal dispersions as a function of surface charge density has been examined only recently [50, 51].

The importance of the change in rheological properties was examined as layer number increases. As the number of polymer layers on the surface increases, the effective volume fraction, and thus the viscosity also increases. The conditions for flocculation also change. It is important to understand how the rheological properties can be affected by adding polyelectrolyte layers if the particles are to be used as drug delivery devices or for the adsorption of toxins.

CHAPTER 2 MATERIALS AND METHODS

Introduction to Materials: Biomedical Applications

SiO_2 is used for a variety of biomedical applications. This material is used as filler in dental composites, in nanostructured materials and coatings for biomedical sensors [52], for coatings on hip replacements, and coatings with antibacterial activity.

Nanoporous SiO_2 is also used in biomedical applications. SiO_2 particles are known to have a high binding capacity for DNA [53], and it is possible to put entire genes into nanoporous SiO_2 . One can envision using these SiO_2 particles as vectors for targeted drug or DNA delivery [54]. Since SiO_2 has a negative surface charge at $\text{pH} > 3$, this material is a good candidate to model a drug delivery system with electrostatic interactions.

Materials

The SiO_2 particles used in this study were nearly monodisperse of approximately $1.5 \mu\text{m}$ in diameter (d_{50} value) with a specific surface area of $2.19 \text{ m}^2/\text{g}$ [39]. The purity and density of the powder were 99.9% and $2.1 \text{ g}/\text{cm}^3$, respectively. SiO_2 particles were provided by Geltech Corporation and were used as received. Sizing of the SiO_2 particles was performed using the Coulter LS230 at $\text{pH} = 9$ so that the SiO_2 particles were completely dispersed. Poly(diallyldimethylammonium chloride) (PDADMAC), $M_w < 200,000$, and poly(sodium 4-styrenesulfonate) (PSS), $M_w = 70,000$, were purchased from Aldrich and were used as received, at 20% wt and 30% wt in water, respectively. PDADMAC and PSS repeat units are shown in Fig. 3-1. As stated earlier, the charged

polymers model charged species such as proteins, DNA, and some biological drugs used to remove toxins. The SiO₂ nanoparticles (19% wt SiO₂ suspension in water, diameter = 13 nm as determined from TEM) were provided by from Nissan Chemical Industries, Ltd. The water used in all experiments was high-purity deionized water prepared in a three-stage Millipore Milli-Q Plus 185 purification system and had a resistivity of 18 MΩ/cm. All experiments in this work were conducted in the absence of any added salt and under the natural pH of the system. All centrifugations were conducted for 15 minutes at 8000 rpm (14400g).

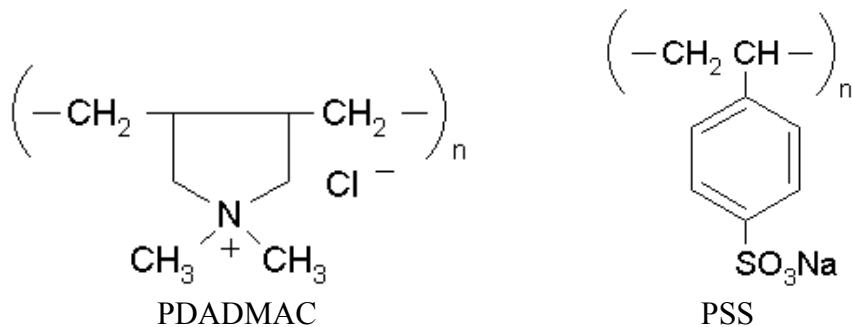


Figure 2-1: Chemical structures of PDADMAC and PSS repeat units.

Study of PDADMAC Adsorption

The multilayers of charged polymers were formed by alternating adsorption of polycations and polyanions. Since SiO₂ has a negative surface charge at the conditions used, the PDADMAC was the first layer to be adsorbed. In order to understand the properties and structure of what is made, an investigative study was done. This study began with determining the adsorption development of PDADMAC on SiO₂ particles.

All adsorption experiments were conducted at room temperature (25°C) using suspensions of 2% vol SiO₂, with no salt added. The SiO₂ particles were added to varying polyelectrolyte dosages using a 1-g/L aqueous PDADMAC stock solution.

Depending upon the polymer dosage, the PDADMAC stock solution was diluted with high purity deionized water to the desired concentration and used as the suspending fluid. The required mass of dry particles was slowly added to the PDADMAC solution. After addition of particles, the suspensions were ultrasonicated for eight minutes and left on a Burrell Model 75 wrist shaker for 15 minutes in order for equilibrium and maximum adsorption to be reached. Ultrasonication and shaking ensures a uniformly charged surface on the core SiO₂ particles by exposing the entire surface to the polycation. After equilibration, the samples were centrifuged. The supernatant was stored in a refrigerator and later used for analysis by Tekmar-Dorhman Phoenix 8000 Total Organic Carbon (TOC) analyzer. TOC measurements were made on the Tekmar-Dorhman Phoenix 8000 TOC Analyzer utilizing UV light and chemical oxidation techniques to break down species containing organic carbon (such as polymers or surfactants) to CO₂ which is then analyzed using a non-dispersive infra-red (NDIR) detector for quantification. The instrument can analyze samples containing as little as 2 ppb carbon.

Kinetics of Adsorption

Another important part of preparing multilayered particles for use in drug delivery is the time of adsorption. Whether the layered particles will be adsorbing toxins in the body or releasing drugs, kinetics and diffusion are very important to understand. In biomedical applications, it is vital to know how long the drugs or other materials will be in contact with the cell membranes or how quickly the particles can adsorb substances harmful to the body. To study the kinetics of adsorption, all dispersions were prepared at a polymer dosage of 6 mg/(g solids). The required mass of dry particles was slowly added to the PDADMAC solution, and the suspensions were sonicated for five minutes and left on the shaker for times ranging from 0 to 180 minutes. The samples were then

centrifuged and the supernatant removed. The residual polymer solutions were stored in a refrigerator and later used for residual carbon analysis. The TOC helped to determine how much polymer was adsorbed on the surface of the particles, and then a correlation between time and concentration were made.

Adsorption Isotherm

Also important is to determine the adsorption density of the polymer on the surface. The molecular weight as well as chemical structure of the polyion can affect the density of the polymer on the surface. It has been well established that adsorbed concentration as well as ionic strength can affect the morphology on the surface [7, 16, 35, 55]. After centrifugation, the supernatants were analyzed for organic carbon. Using a dilution factor of 100, high-purity deionized water was used to dilute the residual solutions. The TOC calibration produced an acceptance criteria of $R^2 = 0.99972$ for aqueous solutions of PDADMAC.

Electrophoretic Mobility (EPM) Measurements

A practical method for determining if the surface charge of the SiO_2 particles has changed after adding the cationic polyelectrolyte into the system is to use electrophoretic mobility (EPM) measurements. Electrophoretic mobility is the rate of migration per unit of electric field strength of a charged particle in a solution under the influence of an applied electric field. From the EPM measurements, the zeta potential, or electric potential at the shear plane, can be determined. The shear plane (slipping plane) is an imaginary surface separating the thin layer of liquid bound to the solid surface and showing elastic behavior from the rest of liquid showing normal viscous behavior. The net charge at the particle surface affects the ion distribution in the nearby region, increasing the concentration of counterions close to the surface. Thus, an electric double

layer is formed in the region of the particle-liquid interface. Figure 2-2 shows this double layer and where the zeta potential originates. This double layer (upper part of figure) consists of two parts: an inner region that includes ions bound relatively tightly to the surface, and an outer region where a balance of electrostatic forces and random thermal motion determines the ion distribution. The potential in this region, therefore, decays with increasing distance from the surface until, at sufficient distance, it reaches the bulk solution value, conventionally taken to be zero. This decay is shown by the lower part of the figure and the indication is given that the zeta potential is the value at the surface of shear [56].

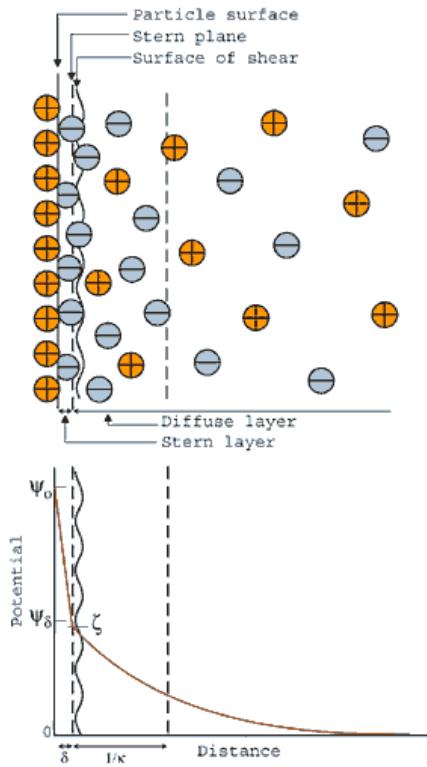


Figure 2-2: A schematic of the double layer and ion distribution on a particles surface (upper part of figure), and a depiction of the zeta potential at the shear (lower part of figure).

Electrophoretic mobilities of the bare SiO₂ and PDADMAC-coated SiO₂ particles were measured using a Zeta Reader Mark 21 at 25°C with no salt added. The apparatus

transforms the electrophoretic mobility u ($\text{m}^2/\text{V}\cdot\text{s}$) into a ζ -potential (mV) by using the Smoluchowski relation

$$\zeta = u\eta/\varepsilon \quad (5)$$

where η (Pa·s) and ε (C/m·V) are the viscosity and permittivity of the solution, respectively. Measured amounts of dry SiO_2 were added to the 1-g/L PDADMAC stock solution to achieve a range of dosages. The 0.05% vol dispersions of the bare SiO_2 and the 0.05% vol dispersions of the PDADMAC-coated SiO_2 were sonicated for three minutes to break up any aggregates and left on the shaker for 30 minutes to ensure equilibrium and complete PDADMAC adsorption before the measurements were made.

Desorption Study

For either drug delivery or toxin removal, desorption of the polymer layers is important to understand. If drugs are to be incorporated into a multilayered particulate system, they must remain adsorbed until the external parameters change and they can be released. Desorption behavior is a crucial part of achieving safe and effective time released drug delivery systems. For toxin removal, the multilayers must stay intact while in the body and adsorbing toxins. For these desorption studies, dispersions of 2% vol were prepared at a polymer dosage of 15 mg/(g solids), ultrasonicated for five minutes and left on the shaker for one hour. The samples were centrifuged and the supernatant removed. The residual polymer solutions were stored in a refrigerator until analyzed by TOC. High-purity deionized water was added to redisperse the samples in 2% vol dispersions. The samples were ultrasonicated for five minutes, left on the shaker for one hour, and centrifuged again. The multiwashing steps were repeated up to five times.

Study of PSS Adsorption

In order to achieve multilayers, an anionic polyelectrolyte is used, PSS. After centrifugation and removal of residual PDADMAC, the particles were suspended in a solution containing 15 mg/(g solids) of PSS polymer. After addition of the particles, the 2% vol suspensions were ultrasonicated for eight minutes and left on a Burrell Model 75 wrist shaker for one hour to ensure complete polyanion adsorption onto the PDADMAC-coated SiO_2 particles. Excess polyelectrolyte was removed after centrifugation.

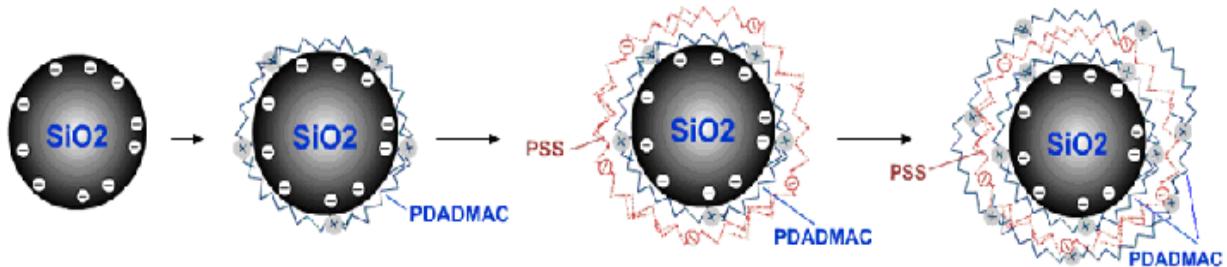


Figure 2-3: Schematic showing the layer-by-layer adsorption of PDADMAC and PSS on SiO_2 core particle.

Rheology

While the rheology of suspensions of hard spheres seems to be rather well understood by now [39, 44, 57, 58], the flow behavior of particles stabilized by multilayers of long polymer chains is still in need of further investigation. Rheological studies of multilayered particles is a novel idea. Depending on the application of the particles, they will be influenced by external forces. One of these forces, shear, is easily induced in processing as well as for quality purposes. The rheology measurements can give an idea of the physical properties of the particles. Environments where the multilayered particles will experience shear are the bloodstream, processing conditions, and perhaps, while being injected into the body. No one has shown the effects of shear as layer number and composition changes. The rheological study performed involves each

the PDADMAC and PSS layers. Both polyions have different molecular weights, chain lengths, and chemical structures. These factors will have an affect on the particle-particle interactions as well as over long-range hydrostatic interactions. Rheological measurements are how to quantify these affects.

Properties of Suspensions for Rheological Studies

Since the rheological properties of suspensions vary over an extremely wide range depending upon volume fraction of the particles, shear rate, and particle-particle interactions [59], different kinds of rheological instruments must be used to determine the viscosity of the suspensions at different shear rates and volume fraction of the particles. Since deviations from homogeneity (e.g., phase separation) and sedimentation of the particles can lead to serious errors, it is most important to make sure the samples have been ultrasonicated and left on the shaker for a suitable time period. The method used to determine the rheological properties of suspensions depends on the characteristics of the material to be studied. From the rheological point of view, suspensions can be classified as follows [60]:

1. Dilute, low viscosity stable suspensions (viscous fluids)
2. Concentrated, high viscosity stable suspensions (viscoelastic fluids)
3. Solid suspensions (elastic solids)
4. Flocculated and coagulated suspensions (viscoelastic fluids with time dependent properties)

The state of a suspension at rest is determined by a balance between the Brownian motion of the particles and interparticle forces. The suspension is considered to be dilute if the Brownian motion is dominant and concentrated if particle-particle interactions predominate [58].

Preparation of Suspensions for Parallel Plate Method

All SiO₂ suspensions were prepared at room temperature (25°C) with 50% vol of solids, with no salt added. PDADMAC was the first layer to be deposited on the SiO₂ core particles. The SiO₂ particles were added to varying polyelectrolyte dosages using a 30- and 60-g/L aqueous PDADMAC stock solution. Depending upon the polymer dosage, the PDADMAC stock solution was diluted with high purity deionized water to the desired concentration and used as the suspending fluid. The required mass of dry particles was slowly added to the PDADMAC solution. After addition of particles, the suspensions were ultrasonicated for 30 minutes and left on a Burrell Model 75 wrist shaker for 24 hours in order for equilibrium and maximum adsorption to be reached. Ultrasonicating and shaking ensures a uniformly charged surface on the core silica particles by exposing the entire surface to the polycation. Using Paar Physica UDS 200 rheometer, at 25°C, viscosity as a function of shear rate was measured at increasing PDADMAC dosage, 0 to 20 mg/(g solids).

PSS was added as the second layer onto the PDADMAC-coated SiO₂ particles. After centrifugation and removal of residual PDADMAC, the particles were suspended in a solution containing 15 mg/(g solids) of PSS polymer. After addition of the particles, the 50% vol suspensions were sonicated for 30 minutes and left on a Burrell Model 75 wrist shaker for 24 hours to ensure complete polyanion adsorption onto the PDADMAC-coated SiO₂ particles. Excess polyelectrolyte was removed after centrifugation. All samples were sonicated for five minutes prior to running the rheometer. Only 15 mg/(g solids) PSS was used for viscosity measurements.

Parallel Plate Rheological Measurements

The Paar Physica UDS 200 is a rotational rheometer that can be used to measure shear viscosity, viscoelastic functions, creep, and yield stress of materials using different geometries such as cone-and-plate, parallel-plate, and concentric cylinder. Tests can be performed under controlled "shear rate" or controlled "stress." In this study, the parallel-plate geometry is used and the temperature controlled at 25°C. The sample is loaded into the space between the two plates. One of the confining surfaces is held stationary, while the other one is made to rotate. The applied torque required to turn the rotating plate is measured.

This method will be used to determine differences in viscosity and storage and loss moduli as the layer composition changes. Changes in viscosity should be seen since the effective volume fraction of the particles is increasing. Changes in storage and loss modulus will give an idea of any structural organization, such as gelation, that may be occurring.

Measurement of Adsorption Layer Thickness of PDADMAC

Adsorbed layer thickness, δ_h , is dependent on polymer chemistry, chain length, ionic strength of the solvent, pH, and the ionic strength of the polyion. The thickness of the polymer layer changes the properties of the particles, such as viscosity, and can affect the applications and processing limitations. The modification of the viscosity by an adsorbed layer of a surfactant or a polymer can be modeled in terms of an appropriate increase δ_h of the radius a of the particles. This leads to the increase in the volume fraction, ϕ , of the particles, which is related to the viscosity of the suspension through Einstein's equation [61]:

$$\mu/\mu_0 = 1 + k\phi \quad (6)$$

where μ (Pa·s) is the viscosity of the suspension and μ_0 (Pa·s) is the viscosity of the liquid phase. Einstein determined a k coefficient equal to 2.5, which is only valid for an infinitely dilute suspension. The SiO_2 particles in this study have a radius of 0.75 μm , and are considered fine, so it is necessary to determine the value of k , Einstein's coefficient.

Other methods of determining the adsorbed layer thickness of a polymer on colloids are reported in the literature. Small-angle neutron scattering (SANS) [62], small-angle x-ray scattering (SAXS) [63], TEM [32], x-ray reflectivity [24], and uv-vis absorbance [21]. All of these methods require the knowledge of complicated equipment and derivations. In this work, the relationship between changes in relative viscosity due to the addition of the polyions is used (Einstein's equation) as well as radius of gyration (R_g) calculations.

Preparation of suspensions for glass capillary method

Two sets of suspensions were prepared for the glass capillary method. The first, a series of stable SiO_2 suspensions (SiO_2 and deionized water) exhibiting various volume fractions up to 20% vol SiO_2 were prepared. After ultrasonication and shaking for 24 hours, the viscosities (μ) were determined.

The second set of suspensions contained SiO_2 particles and varying PDADMAC concentrations up to 4% vol SiO_2 . The SiO_2 particles were added to varying PDADMAC concentrations. Depending on the dosage, the PDADMAC stock solution was diluted with high purity deionized water to the desired concentration and used as the suspending fluid. Several suspensions were prepared at a natural pH of 3 with various PDADMAC

concentrations ($MW < 200000$). After ultrasonication and shaking for 24 hours, the viscosity of the suspensions (μ) and of the corresponding mother liquors (μ_0) were measured.

Glass capillary rheological measurements

The glass capillary method was used to determine the adsorbed layer thickness of PDADMAC on SiO_2 particles. The glass capillary method has been shown to be an effective method of determining the viscosity of dilute stable suspensions over a wide range by varying the capillary diameter [64]. In this simple technique, the time required for a given volume of sample to flow through the length of the capillary, from point A to B, under its own hydrostatic head is measured.

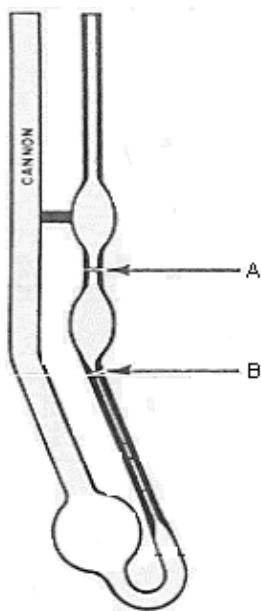


Figure 2-4: Cannon-Fenske glass capillary viscometer.

Flow (efflux) times, t (s), are related to the viscosity of the sample by an equation of the form

$$\mu/\rho = v = at + b/t \quad (7)$$

where μ (cP) is the dynamic viscosity, ρ (g/cm³) is the density of the fluid, v (is the kinematic viscosity (cSt), and a (cSt/s) and b are instrument constants. The last term in the above equation is related to the kinetic energy correction which is negligible for flow times over about two minutes.

The liquid in the bulb above the capillary provides the driving force, and since the height change is relatively small, pressure changes are small during the test. Glass capillary viscometers are usually used for low viscosity samples. Capillaries of different diameters are used for different viscosity ranges to keep flow time through the capillary in the range of 2-5 minutes. In this case, one capillary diameter was used.

Before the measurement was made, the capillary was cleaned of all debris and dried with compressed air. After the sample was suctioned into the glass capillary up to the appropriate line, the glass capillary was immersed in a constant temperature bath of 25°C. After waiting five minutes to allow for temperature equilibration and no bubbles were present, the timer was started and stopped when the sample reached the appropriate marks on the glass capillary. This procedure was repeated three times. Since all the readings were within 180-360 seconds, only one glass capillary was used.

The viscometer calibration constant was multiplied by the average time (in seconds) to determine the kinematic viscosity, v , of the sample by using the above equation with $b = 0$. The kinematic viscosity was then multiplied by the density of the suspension, ρ , shown in Eqn. 8. to determine the relative viscosity, μ .

$$v = \mu/\rho \quad (8)$$

Effective volume fraction (EVF) calculations

The adsorbed polymer creates a coating on the surface of the particle with a significant thickness and therefore, the particles have an effective radius, a_{eff} , that is larger than the radius of the core particles. These systems may be treated as hard spheres if an effective volume fraction is used instead of the core volume fraction of the particles [57]. Effective volume fraction (EVF) is defined as [41]

$$\phi_{\text{eff}} = \phi(a_{\text{eff}}/a)^3 \quad (9)$$

where ϕ_{eff} is effective volume fraction, and ϕ is the core volume fraction of the particles.

In the case of sterically stabilized suspensions, a_{eff} may be written as [41]

$$a_{\text{eff}} = a + \delta \quad (10)$$

where δ (nm) is the adsorbed layer thickness.

R_g (Radius of Gyration) Calculations

One method to calculate the adsorbed layer thickness without making experimental measurements, is to use the radius of gyration, R_g, of the polymer. The R_g is the measure of the end-to-end distance a polymer chain. Therefore, the thickness of the monolayer of polymer on the surface of the SiO₂ particles should be close in value to the R_g. R_g, however, depends on the solvent, the temperature, the molecular weight, and chemical composition of the polymer. Depending on the conformation of the polymer on the surface, the R_g may or may not be a good predictor of adsorbed layer thickness. By using the equations

$$r^2 = NL^2 \quad (11)$$

and

$$R_g^2 = r^2/6 \quad (12)$$

the R_g can be estimated. N is the number of segments in the polymer chain and depends on the molecular weight and chemical structure. L is the length of each segment, or the persistence length. Persistence length is the average projection of the end-to-end vector on the tangent to the chain contour at a chain end in the limit of infinite chain length. The persistence length is the basic characteristic of the worm-like chain [65]. Tricot [66] reports a persistence length of 27 Å for PDADMAC (MW = 250,000 g/mol). This is not the molecular weight of the PDADMAC used in this work, so the calculated R_g will be an approximation.

Study of NanoSiO₂ Layer

In this work, the nanoSiO₂ represents charged drugs that can be delivered to the body's cells. For toxin removal, by incorporating nanoparticles as one of the layers, there is an increase in surface area as well as surface energy. Adsorption of toxins should increase due to the addition of a monolayer of nanoparticles. After removing excess PDADMAC from the PDADMAC-coated SiO₂ suspension, a 25-g/L solution of ultra pure water and nanoSiO₂ was added. In order to confirm that the nanoSiO₂ was adsorbed onto the positively charged surface, zeta potential measurements were made using the Colloidal Dynamic Acoustosizer IIs. The Colloidal Dynamics Acoustosizer uses the Electrokinetic Sonic Amplitude (ESA) effect. Charged particles in suspension are forced to move by an oscillating electric field to produce acoustic compression waves (i.e., sound waves at the frequency of the excitation). Changes in density as the particles move towards and away from the electrodes generate acoustic waves at the surface of the electrodes as an echo of the excitation. The amplitude of the acoustic response is proportional to the velocity of the particle caused by the electric field. The velocity is proportional to the electric field amplitude. The "constant" of proportionality is the

dynamic mobility, which can be shown to be a function of particle size, zeta potential, frequency, and phase lag of the particles velocity relative to the excitation frequency. This relationship is used to extract the particle size and surface charge (zeta potential) from measurement of the ESA. The advantage of this technique is that it can be applied to very concentrated suspensions (up to 40 vol%).

After the zeta potential measurements were conducted, scanning electron microscopy (SEM) was used to determine any changes in surface structure of the layered particles.

CHAPTER 3 RESULTS AND DISCUSSION

Adsorption of PDADMAC

Kinetics of adsorption was studied to determine the time it takes for complete adsorption of PDADMAC onto the surface of the SiO₂ particles to occur. Fig. 3-1 shows the results from this kinetics study. Adsorption density of the polymer was determined as a function of time for samples prepared using a polymer dosage of 6 mg/(g solids). After mixing the particles with the polymer solution, samples were ultrasonicated for five minutes and then left on a shaker for a given period of time, ranging from 0 to 180 minutes. An adsorption density of 0.4 mg/m² is reached in less than 30 minutes. The time of centrifugation and ultrasonication are included in the final time of adsorption. The adsorption density varies by less than 0.1 mg/m², but shows a steady plateau around 0.4 mg/m². The shape of the kinetic curve is typical: a linear increase, which ends rather abruptly. This study shows that the polycation completely adsorbs to the SiO₂ surface very quickly. In the fabrication of multilayers adsorbed onto colloids, additional aspects have to be considered: competing with the formation of a defined monolayer around the particle is the process of coagulation of partly covered particles. The corresponding timescales of adsorption and coagulation are crucial for successful multilayer formation on single colloids, as seen from the following: the rate of polymer chain adsorption (s/m²) onto a particle is given by [67]:

$$k_{\text{ads}} = 4\pi R_{\text{pa}} D_{\text{pol}} c_{\text{pol}} \quad (13)$$

using the assumption of an irreversible and diffusion controlled adsorption. R_{pa} (Å) is the radius of the particle, D_{pol} (m²/s) is the polymer diffusion coefficient, c_{pol} (mg/mL) the polymer concentration. The competing process, the rate of collisions (s/m²) between particles, can be described

$$k_{\text{coll}} = 4\pi R_{\text{pa}} 2 D_{\text{pa}} c_{\text{pa}} \quad (14)$$

with D_{pa} (m²/s) and c_{pa} (mg/mL) as the diffusion coefficient and concentration of particles, respectively. The factor 2 takes into account the fact that both objects are diffusing. The requirement of a fast chain adsorption is thus fulfilled if the polymer concentration is large compared to the particle concentration.

For medical composite systems like drug delivery processes, if charged species are used and electrostatic interaction is the mechanism of adsorption, it is important to understand the kinetics of this charged process, whether it be for the process of adsorbing toxins or processing the multilayered systems. For removing toxins, the process of adsorbing charged chemicals or molecules must be quick in order to avoid the death of cells.

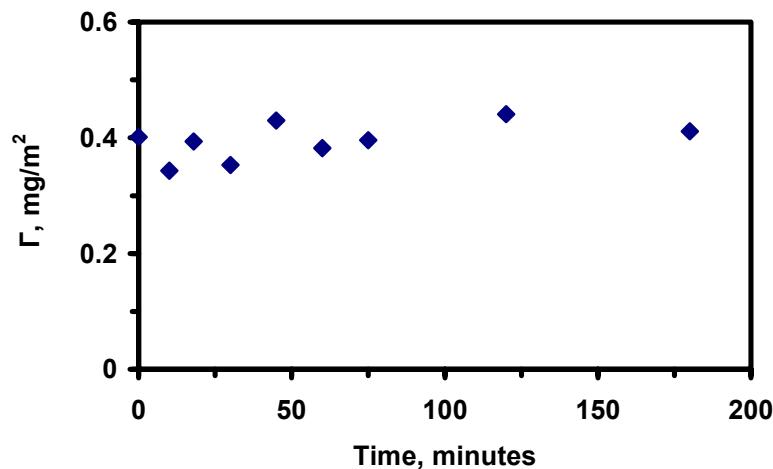


Figure 3-1: Adsorption density as a function of time for SiO₂-PDADMAC system (25°C, pH = 4.58).

For the 2% vol SiO₂ suspension containing PDADMAC ($M_w < 200,000$ g/mol), an adsorption isotherm was determined by analyzing the initial solution and the residual solution removed after centrifuging. The adsorption isotherm for SiO₂ suspension containing PDADMAC can be seen in Fig. 3-2. This curve has a typical shape with a very steep increase at extremely low C_{eq} , followed by a saturation plateau where Γ is nearly independent of concentration. Γ is the adsorption density of the polycation adsorbed on the surface of the particles. The residual solution was tested for organic carbon by TOC measurements. In Fig. 3-2, coverages approaching 0.5 mg/m² were observed at high concentrations of PDADMAC, on the apparent plateau of the isotherm. At the surface of the SiO₂, the average interfacial conformation of the PDADMAC chains may be changing with coverage to include some segments that are loosely attached to the surface, as small tails or loops. This may result from repulsions within the adsorbed layer, which can be long range at the low ionic strength [55]. When increasing the amount of polymer added to the system, giving higher coverages above 0.6 mg/m², the ionic strength is increased by ions brought along with the polymer. The increase in ionic strength resulting from the additional polymer in the system may screen long-range electrostatic repulsions, allowing chains to approach more closely or adsorb more flatly with decreased mobility [42]. The amount of polyelectrolyte adsorbed depends on the charge density of the surface, σ , as well as the pH and ionic strength of the solution. The σ and charge density along the chain, and the pH and ionic strength are dominating parameters for polyelectrolyte adsorption to hard surfaces. In this study, the pH and ionic strength were not adjusted. Therefore, the flexibility, morphology, thickness, and transport properties of the monolayer depends on the chemical structure, MW, and

amount of polyelectrolyte adsorbed. Error analysis of this study included preparing three samples for each point and each sample was analyzed three times. The error calculated was negligible on the plot presented.

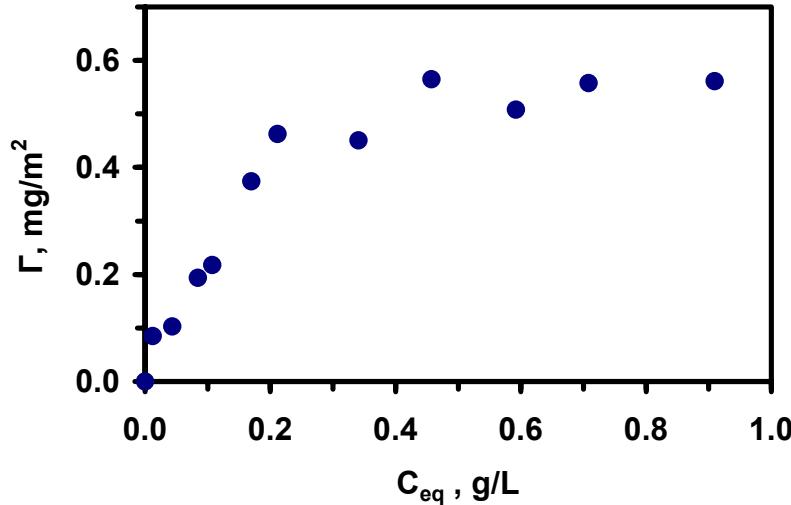


Figure 3-2: Adsorption density as a function of equilibrium concentration of PDADMAC onto the surface of SiO_2 particles (25°C , $\text{pH} = 4.58$).

The zeta potential is a measure of electrostatic interactions between solid particles covered by polymer layers, and its magnitude depends on the adsorbed concentrations. The magnitude of the zeta potential gives an indication of the potential stability of the colloidal system. Literature reports that the SiO_2 surface charge is dependent on the pH value and the electrolyte concentration. At $\text{pH} > 3$, SiO_2 has a negative surface charge, and the surface becomes more negatively charged with increasing pH. In the case of bare SiO_2 , there is a plateau in basic solution, and the point of zero charge, near $\text{pH} = 3.0 - 3.5$ [42]. The bare SiO_2 particles are well dispersed above $\text{pH} = 3$, and the negative charge of the SiO_2 surface will allow for electrostatic adsorption of the PDADMAC onto the SiO_2 core particles. At a $\text{pH} < 3$, the surface of the SiO_2 particles will have a positive charge, and a PDADMAC monolayer will not form based on electrostatic forces.

Fig. 3-3 represents zeta potential as a function of PDADMAC dosage and, as can be observed, the magnitude of zeta potential increases as more polymer is adsorbed onto the surface of SiO_2 particles. As shown in Fig. 3-3, zeta potential will reach a plateau at a polymer dosage of 10 mg/(g solids). This dosage corresponds with the adsorption density of 0.5 mg/m², shown in Fig. 3-2.

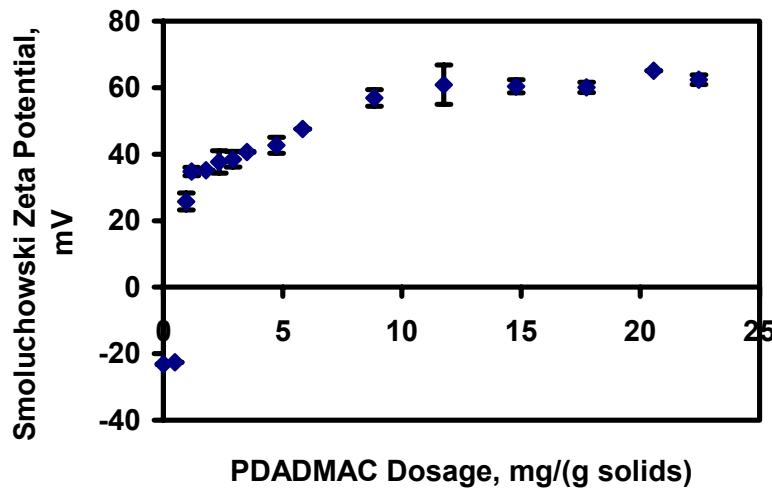


Figure 3-3: Zeta potential as a function of polymer dosage for SiO_2 -PDADMAC system (25°C, pH = 4.58).

Both figures indicate that maximum saturation of the 1.5- μm SiO_2 particles, in natural pH and ionic strength conditions, occurs at an adsorption density of 0.5 mg/m² of PDADMAC. Increasing the amount of polymer stabilizes the dispersion, and none or only very weak repulsive forces exist in such a case. The zeta potential also increases but begins to level off around +62 mV. Optimal flocculation in salt-free environments is observed at the isoelectric point ($\zeta = 0$). The plateau indicates a complete saturation of SiO_2 core particles with the polycation above 10 mg/(g solids). For error analysis four samples for each point were analyzed four times due to the sensitivity of the TOC analysis. The error was negligible the on the plot presented. Particles with zeta

potentials more positive than +30 mV are normally considered stable, and at a zeta potential of +62 mV, the surface of SiO₂ is completely covered with the PDADMAC.

Desorption of PDADMAC and PSS

To study the desorption of PDADMAC from the surface of SiO₂ particles, samples were centrifuged and re-dispersed in pure water several times. The supernatants were analyzed for desorbed carbon using a TOC analyzer. The bare SiO₂ particles were mixed with a concentration of 0.63 g/L of PDADMAC. The supernatant removed after the first centrifugation contained 0.57 g/L of PDADMAC, shown in Fig. 3-4, leaving 0.06 g/L PDADMAC on the surface of the SiO₂ particles. After adding deionized water, redispersing the PDADMAC-coated particles, and centrifuging again, the desorbed PDADMAC in the supernatant is measured using TOC up to five times. This study indicates that after centrifuging and washing with water, the PDADMAC was not removed from the surface of the SiO₂ particles. Preliminary TOC measurements on the desorption of PSS produce similar results. After centrifugation, not all of the PSS was removed from the solution. PSS remained on the surface of the PDADMAC-coated SiO₂ particles. EPM measurements also supported this observation.

The polymer layers must remain intact throughout the processing procedure. Excess polyion in solution is removed through physical means and washing with pure water. The electrostatic interaction between the layers and the surface of the SiO₂ is very strong. For a drug delivery system, however, the layers of polymer should be released due to changes in external parameters, such as pH, glucose concentration (for diabetes), or even high toxin levels. These parameters will have to be looked at in regards to the diffusion of the polymers away from the surface of the particles.

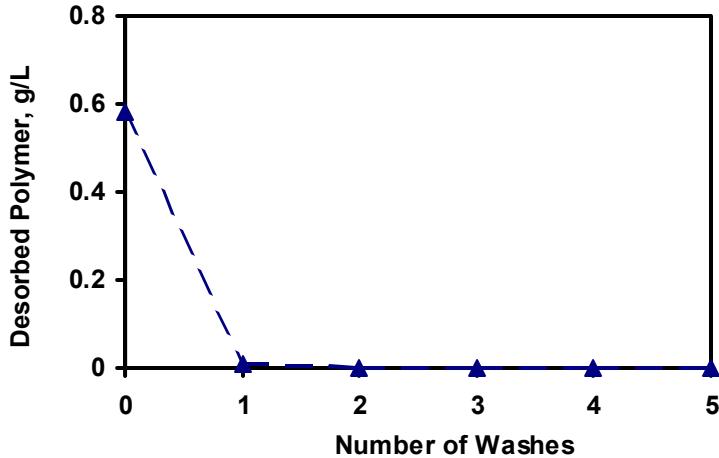


Figure 3-4: Desorption study of PDADMAC on SiO_2 particles after centrifuging and washing with deionized water.

Zeta Potential

EPM measurements were conducted to follow the assembly of the PDADMAC/PSS multilayers onto the surface of SiO_2 particles. In the absence of polymers, SiO_2 samples exhibited a zeta potential of nearly equal to -23 mV in pure water ($\text{pH} = 5$). The zeta potential of the SiO_2 particles can be altered, depending on whether a polycation or a polyanion is adsorbed as the outermost layer [32]. The zeta potential of each layer is shown in Fig. 3-5. The zeta potential of the PDADMAC layer was +64 mV, a value consistent with the outermost layer being a polycation. The assembly of the second layer of PSS caused a reversal in sign of the zeta potential, from +64 mV to -42 mV, an indication that the outermost layer is a polyanion. This reversal in sign occurred up to four total layers on the surface of the SiO_2 core particles, ending with a negative zeta potential, or PSS.

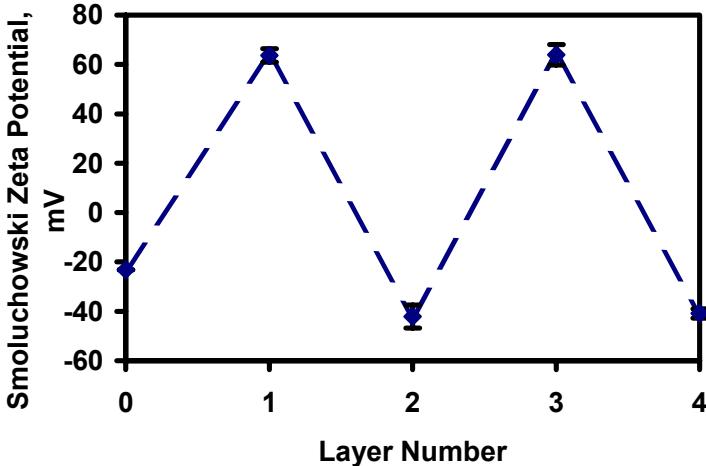


Figure 3-5: Zeta potential measurements showing the change in surface charge as PDADMAC (Layer Number 1), PSS (Layer Number 2), PDADMAC (Layer Number 3), and PSS (Layer Number 4) are added (25°C, pH = 4.35, in the absence of salt).

The zeta potential measurements were conducted at a pH ~ 5.3 (above the isoelectric point of SiO_2), bare SiO_2 bears an overall negative charge at this pH. As subsequent adsorption of PDADMAC and PSS layers occurred, the zeta potential exhibited changes from positive to negative, respectively. The zeta potential values were +62 mV when PDADMAC formed the outermost layer and about -42 mV when PSS formed the outer layer on the SiO_2 core particles. Caruso et al. [32] have reported a value of +45 mV for zeta potential when PDADMAC forms the outermost layer in the presence of 0.5 M NaCl in the system. The difference between the zeta potential values is due to the presence of salt in the system used by these investigators. The alternating sign of zeta potentials observed are characteristic of stepwise growth of multilayer films on colloids [14]. A similarly regular zeta potential has been observed after deposition of various polycation pairs. An interesting feature is the fact that the zeta potential oscillates between the same values, with saturation occurring around 60 mV after polycation adsorption, and around -40 mV for polyanion adsorption. This implies that saturation occurs when a

fixed potential is reached, independently of material employed. It provides evidence for the electrostatic repulsion by the outer layer being the mechanism controlling the adsorbed amount, and limiting further adsorption, and not the polyion stoichiometry with respect to the underlying layer.

The silica-water interface contains a variety of silanol groups (Si-O-H) that can ionize to produce negative charges (Si-O⁻). Although the density of surface charges on silica at pH = 5 is quite low, the density of potential counterion sites is high because the silanol protons can exchange for other adsorbed cations [68]. This allows for the polycation adsorption. Additionally, the protonation of the oligomer itself contributes to the ionic strength of the solution. The influence of ions on the coverage in Fig. 3-2, however, cannot be observed since no salt was added to the system.

The increase in ionic strength resulting from the addition of polymer to the system may screen long-range electrostatic repulsions, allowing chains to approach more closely or adsorb more flatly with decreased mobility. The charge of the polyions leads to enlarged polymer coils due to electrostatic repulsion between charged segments. Furthermore, adsorption of polyions onto oppositely charged particles is dominated by electrostatic forces whereby the adsorbed amount depends on shape, size, and conformation of the polyion coils. At low ionic strength, polyelectrolytes with high charge density, such as PDADMAC, tend to adsorb in a planar structure with a large portion of adsorbed trains [69].

As suggested by Schwarz et al. [70], the question remains that to what extent zeta potential and adsorption measurements can be applied to characterize stability or instability of dispersions in the presence of polyelectrolytes. As shown in Fig. 3-4, the

magnitude of zeta potential increases by increasing the amount of polymer in the system. The repulsive forces which are caused by the positive charges of the polycations increase with increasing concentration of polyelectrolyte. This difference in magnitude of the zeta potential can be ascribed to variations in the conformation of the polyelectrolytes at the surface of quartz [71], which may arise from the differences in underlying surface morphology of the particles. The alternating values do qualitatively demonstrate a successful recharging of the particles surface with each polyelectrolyte deposition [68].

Adsorption of polyelectrolytes on oppositely charged surfaces depends strongly on the electrostatic interaction, so the nature and concentration of the salt in solution and the pH of solution may have a significant role. It has been observed that PDADMAC adsorption on the surface of SiO₂ particles increases with KCl concentrations [71]. Bremmell et al. [72] measured forces between SiO₂ surfaces in the presence of a cationic copolymer and 0.1 mM NaCl. They found that the force was purely attractive at low concentrations and repulsive above 50 ppm.

Adsorbed Layer Thickness

Adsorbed layer thickness can be calculated using many methods, as stated earlier. For example, when using UV-vis adsorption spectroscopy or x-ray reflectivity after the fabrication of multilayered particles [2, 24], the observed interference pattern, called Kiessig fringes, can be analyzed to give the overall film thickness as a function of layer number [24, 73]. As with many other systems prepared by this technique, they show that the total thickness of the multilayer assemblies increases linearly with the number of adsorbed layers, indicating a stepwise and regular deposition process. However, using these methods can be difficult and time consuming.

Einstein's equation relates linearly the viscosity of the suspension to the volume fraction of particles in suspension. For dilute solutions (< 4% vol) a k coefficient is equal to 2.5. Fig. 3-6 shows that above 4% vol the suspension begins to deviate from Einstein's equation.

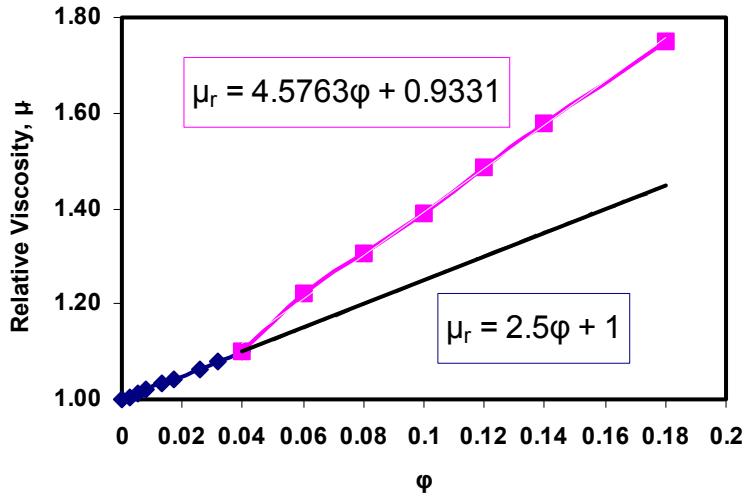


Figure 3-6: Relative viscosities of dispersions versus volume fraction of SiO₂ in water.

In order to determine adsorbed layer thickness for PDADMAC (MW < 200,000), increasing concentrations of PDADMAC were added to the SiO₂ core particles. As expected at a dosage of 10 mg/(g solids) a plateau begins, as shown in Fig. 3-7. From the previous adsorption isotherms and EPM measurements, this value makes sense. Complete coverage of the core particles was occurring. To determine the adsorbed layer thickness of the PDADMAC, a relative viscosity located on the plateau was used for calculations. For a PDADMAC dosage of 12 mg/(g solids), the relative viscosity recorded, 1.1989, corresponds to a volume fraction of 0.050, which amounts to 1.25 times the initial volume fraction, 0.04. As the SiO₂ particle has a radius of 0.75 μm , if the volume fraction is multiplied by 1.25, the radius will be multiplied by $(1.25)^{1/3}$, which is an increase in radius that corresponds to a polymer thickness of 58 nm.

Fig. 3-7 shows the increase in relative viscosity as a function of polymer concentration. It is clear that above 12 mg/(g solids) a monolayer of PDADMAC has adsorbed. The relative viscosity values at PDADMAC concentrations above 12 mg/(g solids) were used to plot the adsorbed layer thickness versus dosage of PDADMAC in Fig. 3-8.

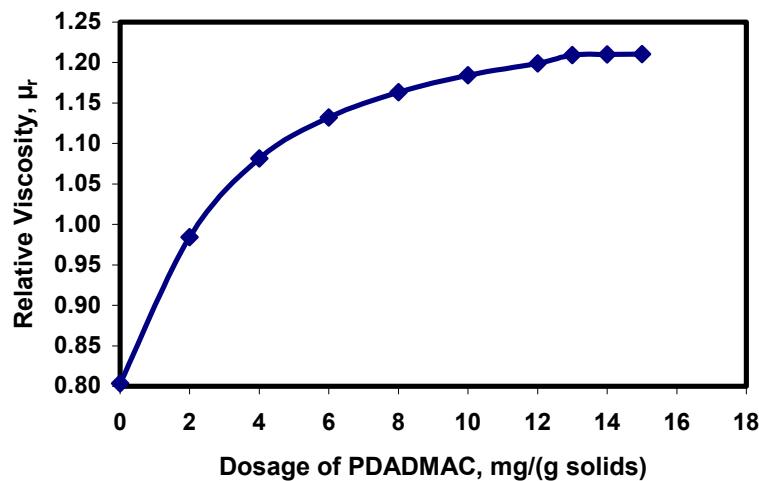


Figure 3-7: Relative viscosity of SiO_2 dispersion versus 200,000 molecular weight PDADMAC dosage.

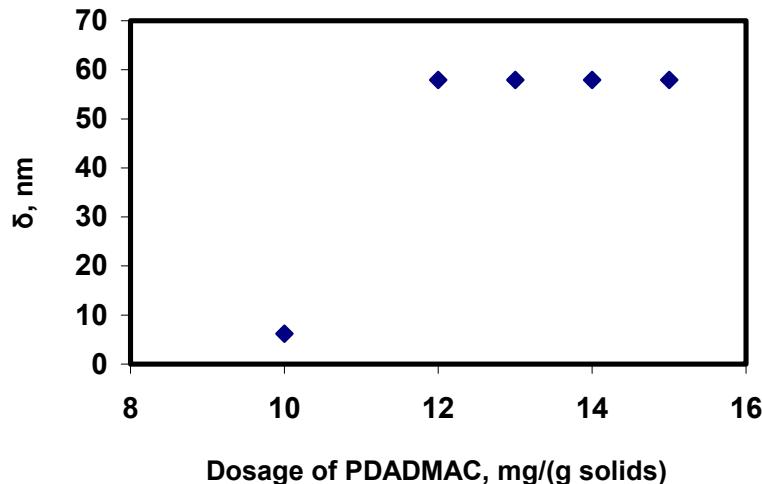


Figure 3-8: Adsorbed layer thickness of PDADMAC on surface of $1.5 \mu\text{m}$ SiO_2 particles, using effective volume fraction calculations, as concentration of PDADMAC increases.

It can be seen that at a critical dosage, a monolayer of PDADMAC is formed. By using the glass capillary and calculating the relative viscosities of the samples, the thickness of the adsorbed layer can be determined.

The persistence length of the 250,000 molecular weight polymer and equations (6) and (7) were used to determine the adsorbed layer thickness. These values are listed in Table 3-1 and are compared with adsorbed layer thickness values obtained using other techniques. The radius of gyration of a polymer is dependent on molecular weight, ionic strength of the solution, temperature, and chain length. Caruso and Möhwald [32] have used single particle light scattering (SPLS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) to determine adsorbed layer thickness of polymer/particle multilayers. They also report an error of 10%.

Table 3-1: PDADMAC adsorbed layer thickness values obtained by various methods.

Layer Number	Layer Thickness (nm)				
	SPLS [32]	SEM [32]	TEM [32]	η_r	R_g
1	24	38	30	58	49

Due to error involved using the instruments and differences in the composition of the core particles, ionic strength, and pH of the systems, deviations from Caruso and Möhwald's work are expected. Caruso and Möhwald used negatively charged polystyrene latex particles of diameter 640 nm, and they adjusted the ionic strength of their PDADMAC solution to 10^{-3} M NaCl and the pH to 5.6. In this work, SiO_2 is the core particle ($d = 1.5 \mu\text{m}$), and the ionic strength and pH (3-4) are not adjusted. Since the values are within the same magnitude, it can be concluded that the glass capillary method can be fairly accurate when determining the adsorbed layer thickness of the PDADMAC on the surface of SiO_2 core particles.

The glass capillary method was used to determine the kinematic viscosity, ν . This method is very sensitive to temperature and dispersion of the particles in the suspending fluid. The samples were ultrasonicated and the particles dispersed well. The error, however, calculated using this method was very small. Many dispersions were run multiple times in order to exclude error in this data.

Rheology of Dispersions of Multilayered Particles

Rheology measurements were made using the parallel plate geometry as PDADMAC concentration increases. Fig. 3-9 shows a distinct increase in viscosity initially at low shear rates. This makes sense because as the PDADMAC is adsorbing onto the SiO_2 surface, the adsorbed layer thickness, and thus the effective volume also increases. At low shear rates the viscosity increases by a factor of 10. In the case of 5 mg/(g solids), the viscosity has the maximum value. In order to explain this behavior, it is necessary to note that complete coverage of the SiO_2 particles does not occur until 10 mg/(g solids) PDADMAC solution is added. Therefore, it can be concluded that at this dosage only part of the SiO_2 particle surfaces are covered. When the particles are only partly covered with polymer, the adsorbed polymer can form macromolecular bridge by adsorbing onto two particles simultaneously. A dosage of 5 mg/(g solids) appears to be the condition for maximum bridging flocculation.

At high shear rates, the bridging structures are broken down due to the high shear. At high shear, the double layer deforms and the effective volume fraction is affected. In Fig. 3-9, the viscosity in all cases shows a decrease at higher shear rates. At low shear rates interparticle forces dominate, whereas at high shear rates hydrodynamic forces dominate.

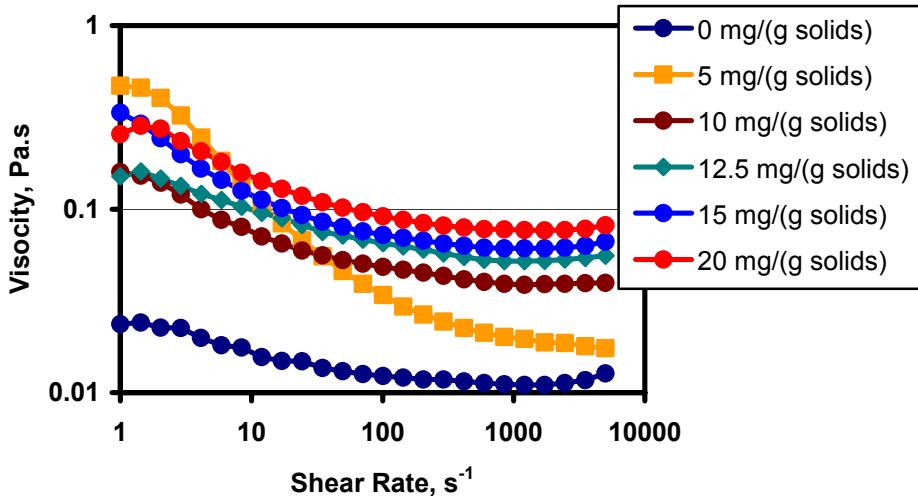


Figure 3-9: Viscosity versus shear rate at increasing dosage of PDADMAC on core SiO₂ particles.

In Fig. 3-10 at a dosage of 5 mg/(g solids) a peak can be seen at low shear rates. As the shear rate increases, this peak gradually disappears, another indication of the optimal conditions of bridging flocculation. At higher shear rates, the particles are dominated by long range hydrodynamic forces. For error analysis, three samples for each point were analyzed three times. The error was negligible to the plot presented.

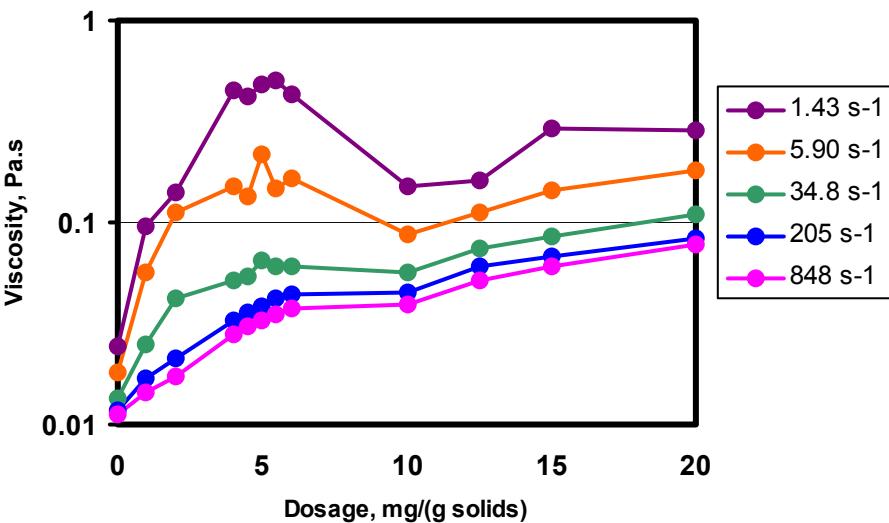


Figure 3-10: Viscosity versus dosage of PDADMAC on core SiO₂ particles as a function of increasing shear rate.

After the second layer, PSS, is added to the surface the effective volume fraction increases again. At low shear rates, the viscosity is 100 times higher, but at high shear rates the viscosities converge. This indicates structure formation at low shear rates. This structure may be a gel formation. At low shear rates, the interaction between the suspended particles is relatively weak and the system is predominantly viscous in nature, while in the region of higher shear, the system becomes predominantly elastic and the adsorbed polymer layers may interpenetrate or be compressed [74].

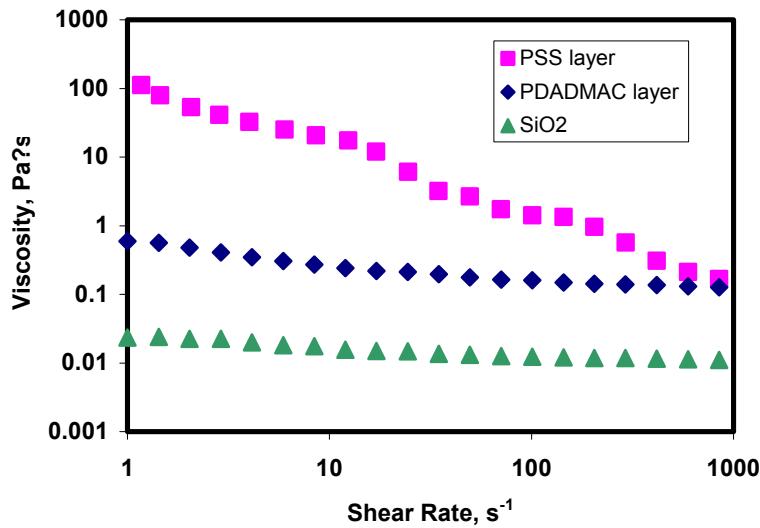


Figure 3-11: Viscosity versus shear rate of core SiO₂ particles, PDADMAC-coated SiO₂, and PSS-PDADMAC-coated SiO₂.

NanoSiO₂

Fig. 3-12 is an SEM picture of 1.5 μm core SiO₂ particles. This picture exhibits well the monodispersity of the core particles. After adding the appropriate concentration of PDADMAC to the dispersion, the particles appear more ordered and less aggregated (Fig. 3-13). The particles become more disperse due to the polyelectrolyte acting as a dispersant. The particles are still monodisperse and appear to have a smooth surface.

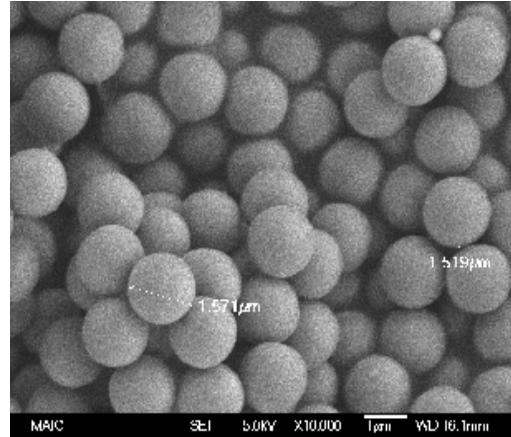


Figure 3-12: SEM of 1.5 μm SiO_2 core particles.

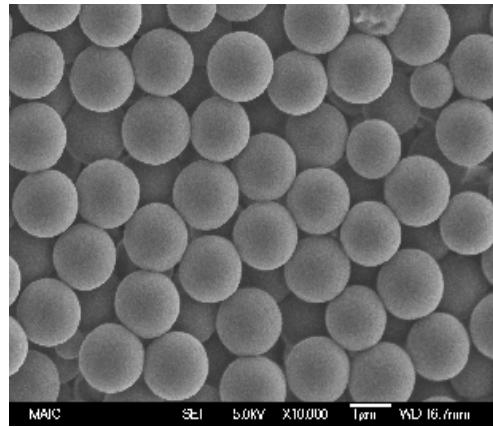


Figure 3-13: SEM of 1.5 μm SiO_2 particles completely covered with PDADMAC (MW = 200,000)

Fig. 3-14 shows the nano SiO_2 adsorbed onto PDADMAC-coated SiO_2 particles.

The surface of the particles appears “rough.” This “roughness” is the nano SiO_2 particles. The particles are also attached and are flocculated. This may be due to the increase in surface energy of the system. As the surface area of the particles increases due to the addition of nano SiO_2 , the surface energy also increases. Future work indicates that this will be a problem for drug delivery and toxin removal systems. The layered particles need to be able to circulate throughout the environment they are in and have maximum surface exposure to be successful in their application. Another reason for the flocculation is that the nano SiO_2 may have been added too quickly. The particles did not have enough

time for steric stabilization to occur. The exposed positive charges of the PDADMAC caused the particles to stick together.

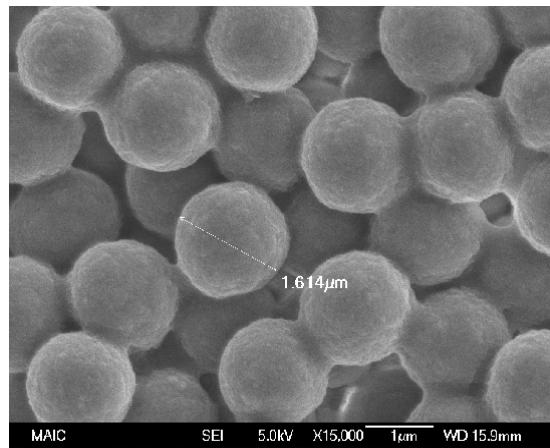


Figure 3-14: SEM of nanoSiO₂ adsorbed onto PDADMAC-coated SiO₂.

CHAPTER 4 SUMMARY AND CONCLUSIONS

In this work, the stability of polycation and polyanion multilayers on SiO₂ were examined, both as a fundamental exercise and as a basis for future quantitative interpretations of adsorbed high-molecular-weight cationic and anionic polyelectrolytes for use in colloid drug delivery systems or toxin removal. The ionic strength and pH was not adjusted, and for all the conditions studied, data for coverages above 0.5 mg/m² were found to show complete polyelectrolyte coverage on the SiO₂ particles for both PDADMAC and PSS. For the natural pH range of our experiments (pH = 4-5), SiO₂ particles had a negative charge. EPM measurements confirmed this behavior. An adsorption isotherm of adsorbed polycation as a function of equilibrium concentration showed a characteristic plateau at 0.5 mg/m². At and above this concentration, the PDADMAC is completely covering the surface of the SiO₂ core particles. The kinetics study further showed that complete coverage and stability of the particle-polymer system occurs in less than 30 minutes. This quick adsorption time makes sense since the PDADMAC has a strong ionic charge when dissociated in water.

This work demonstrates that a homogenous and stable polyelectrolyte, both polycationic and polyanionic, can be adsorbed onto micron-sized SiO₂ core particles in a controlled, stepwise adsorption using electrostatic forces as the basis of motivation. Zeta potential reversal with deposition of each layer was observed. Desorption studies under multiwashing conditions shows stable layered structures. Adsorption isotherms and EPM measurements both verify adsorption of polyelectrolytes onto SiO₂ core particles. The

employment of colloidal particles as templates for the assembly of multilayer shells of inorganic-organic materials through solution adsorption provides a viable route to the production of tailored new materials with unique properties for drug delivery or adsorption of toxins.

Control of stability and bulk rheological properties is an important part of colloid systems. It is also of fundamental interest to understand the relation between the colloidal properties and factors such as interparticle forces, hydrodynamic interactions, and physical and chemical characteristics of the system that govern the dispersion properties [74]. The rheological measurements conducted showed that as the layer number increases, the viscosity also increases. For the PSS layer, there may be a structural organization of the particles at low shear rates that is disrupted at higher shear rates. These measurements showed a large change in the bulk properties of the particles. By adding one and two layers of polymer on the surface of the SiO₂ particle, changes can be observed.

After a stable PDADMAC layer was demonstrated, nanoSiO₂ was added into the system. With no pH adjustments, the nanoSiO₂ have a negative surface charge. It was hypothesized that the nanoSiO₂ should adsorbed onto the PDADMAC-coated SiO₂ particles. Zeta potential measurements confirmed that the nanoSiO₂ was adsorbed onto the surface, but did not exhibit a stable structure on the surface of the layered particles. At a pH of 4.3, the zeta potential of the particles was -14.23 mV. Further characterizations are needed at this point.

SEM pictures indicated that there was a definite change in surface structure of the layered particles. This structure is described as a “rougher” surface as compared to the

PDADMAC-coated SiO₂. The PDADMAC-coated SiO₂ micrographs exhibit very smooth surfaces of evenly dispersed particles. After adding nanoSiO₂ into the layered structure, the surfaces appear “rough,” and the particles are not well-dispersed. The layered particles are sticking together. This indicates that the system cannot be considered stable. The particles cannot be used as single drug delivery systems if they are agglomerated. Further research must be done in order to resolve this issue.

CHAPTER 5 FUTURE WORK

For a number of applications, such as in controlled release or in separation technology, it is of interest whether the properties of polyelectrolyte multilayers can be changed by varying the external conditions, since controllable and tunable properties are required. This concerns, for example, the control of permeation by external parameters. In addition to this, the response of polyelectrolyte multilayers to external parameters can be analyzed in terms of basic information on their internal material properties. For example, swelling experiments provide insight into the interactions within polyelectrolyte multilayers, and thus for example the internal hydrophobicity.

Predicting overall material properties as a consequence of the internal composition and local interactions remains a challenging task. Polyelectrolyte multilayers are complex materials with interesting properties on several length scales. Each layer has its own unique properties, and the multilayered structure creates a three-dimensional structure in which the layers combined create a particle with its own unique properties.

The growth of polyelectrolyte multilayers on colloid particles has been demonstrated and shown to be a fairly simple process. However, from previous SEM pictures, the surface layer on the 13-nm SiO₂ particles does not appear to be stable, in the sense that the layered particles appear to be aggregating. Zeta potential measurements show that the surface charge is consistent with the nanoSiO₂ covering the surface completely (-14.3 mV, pH = 4.3). In order to stabilize this system, the layered particles

cannot be sticking together. Consideration into adjusting the parameters of adsorption should be considered.

Once the nanoSiO₂ is stabilized on the surface, experiments involving toxins found in water as well as other classified bio-toxins. There has also been some work in using nanosupsensions as nanoparticulate drug delivery systems.[75] It would be promising work to begin incorporating drugs into the layers using electrostatics. In order to use the systems is drug deliver, there will also have to be diffusion studies of the polymer layers. The external parameters that affect diffusion rates will have to be determined and stated. Some work regarding the diffusion of polyions in polyelectrolyte multilayers has begun [76].

Further desorption studies in changing pH environments should also be considered. It is known that pH has an important role in the layer thickness, morphology, and surface properties of the polyelectrolyte structures, but it is unknown how is can affect the stability of the layers.

In principle all polyelectrolytes should be suitable for incorporation into multilayer assemblies; and in addition to this, this study has shown the incorporation of nanoparticles as a layer. This implies that there is no principle restriction to polyelectrolyte, and that the construction of multilayer assemblies should also be possible by using charged particles. As an example of such particles we have chosen nanoSiO₂. For future work, the nanoparticles bind to the charged PDADMAC surface and partially penetrates it. It is not known how the stable these nanoparticles are as a layer, as well, whether or not multilayers can be formed on nanoparticles. It may be possible that the next deposition layer, whether it be PDADMAC, a silanol (for silylating the surface), or

another positively charged polymer species (protein, DNA, etc), fills holes between the nanoparticles, and the layer surface restored. Uniform layers of large biomolecules or biomolecular assemblies under controlled conditions can be achieved.

The future, however, of multilayered SiO₂ particles lies in adsorption of toxins, heavy metal ions, and corrosive molecules. By using an adsorbent and layering that adsorbent with nanoparticles increases the surface area as well as the surface energy. These particles would be ideal for adsorption processes and can be studied further. There is much potential in medical composite systems for these layered particles.

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BIOGRAPHICAL SKETCH

I was born in 1980 and grew up in Tampa, Florida. I graduated from Berkeley Preparatory School, Tampa, Florida, in June 1999. I was accepted into the University of Florida and finished my Bachelor of Science in materials science and engineering, specializing in polymers, in the summer of 2003. I continued with my Master of Science, also in materials science and engineering, at the University of Florida. I plan to receive my Master of Science in May 2005.

I met my future husband, Chad Macuszonok, in 1999, and we are planning our wedding for August 2005. This is the beginning of the rest of our lives.