SURFACE CHARACTERIZATION OF SILOXANE, SILSESQUIOXANE, AND MALEIC ANHYDRIDE CONTAINING POLYMERS AT AIR-LIQUID INTERFACES

by

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MASTER OF SCIENCE in Chemistry

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(Abstract)

Langmuir-monolayer formation at the air/water interface (A/W) can be achieved by spreading amphiphilic molecules on a liquid subphase and compressing them into an ordered arrangement. The use of the Langmuir-Blodgett technique (LB) to prepare ultra thin films on solid surfaces from monolayers at A/W has considerable utility for studying surface interactions. In particular, the phase behavior of polyhedral oligomeric silsesquioxanes (POSS) was examined using a combination of LB and Brewster angle microscopy (BAM).

Polymer fillers have been shown to reduce the cost and often improve the properties of high performance polymer composites. The utility of POSS as a potential nanofiller in blends with polymers such as poly(dimethylsiloxane) (PDMS) and poly(vinylacetate) (PVAc) was explored using surface pressure-area per monomer isotherms (\(\Pi-A\)) and BAM. Substantial morphological differences are seen between polymer blends with heptasubstituted trisilanol-POSS and fully condensed octasubstituted-POSS due to differences in subphase affinity.

Several poly(1-alkene-alt-maleic anhydride) (PXCMA) polymers were studied at both the gas/liquid interface as Langmuir films and at the gas/solid interface as Langmuir-Blodgett thin films on silicon substrates. A 0.01 M HCl solution (pH~2) was used during film deposition to ensure the carboxylic acids were fully protonated. The PXCMA polymers included X=1-hexene, 1-octene, 1-decene, and 1-octadecene (represented as PHCMA, POCMA, PDcMA, and PODcMA respectively). The \(\Pi-A\) isotherms of these polymers were consistent with those obtained previously.\(^1\)

Tensiometry was used to determine the critical micelle concentrations (c.m.c.) of variable molar mass poly(dimethylsiloxane-b-(3-cyanopropyl)methylsiloxane-b-dimethylsiloxane) (PDMS-PCPMS-PDMS) triblock copolymers and a
poly(dimethylsiloxane-b-2-ethyl-2-oxazoline) diblock copolymer. Dynamic light scattering (DLS) corroborated interfacial tension results. The polymers exhibited well-defined temperature-independent c.m.c.'s. These measurements ensured that the synthesis of cobalt nanoparticles for biocompatible magnetic fluids occurred above the c.m.c.
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CHAPTER 1

Introduction

1.1 Monolayers

Langmuir monolayers are unimolecular films that exist at the gas/liquid interface, most commonly at the air/water interface (A/W). Benjamin Franklin first demonstrated the concept of spreading monolayers in 1774 by spreading oil on the surface of a pond and noticing that the teaspoon of oil calmed the surface of a half-acre of water.² This experiment was followed roughly one hundred years later by Lord Rayleigh's (John William Strutt) conclusion that maximum oil film extension is representative of a layer one molecule thick.³ At about the same time, Agnes Pockels designed the first instrument that would become the modern Langmuir-Blodgett trough using a wire ring, a simple slide balance, and her kitchen sink.⁴

Irving Langmuir was the first to conduct a systematic study of amphiphilic molecules at A/W in the early 1900's⁵ and Katherine Blodgett was the first to provide a detailed description of the deposition of carboxylic acid multilayers onto solid substrates several years later.⁶ As a result of these two important developments, the technique by which multilayers were made was named Langmuir-Blodgetttry (LB). Over the past fifty years, LB has gained popularity among scientists internationally as its applications have grown to include coatings, optics, sensory devices, and biomembrane research.⁷ To accommodate this growth, the Langmuir-Blodgett trough has evolved from a kitchen sink into a highly advanced instrument that features temperature, compression rate, and deposition control for the study of ordered monolayers and multilayer films.

Monolayers can be used to study the surface properties of both small molecules and polymers. The formation of a monolayer occurs as molecules that are spread on a surface progress through phase transitions including the gaseous, liquid, and solid phases (Figure 1.1). The area per molecule can be defined as the average area occupied by one molecule on the surface at a particular surface pressure. The gaseous phase is characterized by a random arrangement of molecules on the surface with a large area per molecule and low surface pressure. The liquid phase can be separated into two different
Figure 1.1 – Generic Π-A Isotherm for Amphiphilic Molecules

\[ \pi_0 \sim 20-50 \text{ mN} / \text{m} \]

\[ \pi_0 \sim 0.01 \text{ mN} / \text{m} \]

\[ A_0 / \text{nm}^2 \cdot \text{molecule}^{-1} \]
phases for some molecules. A first order transition from the gas phase to the liquid-expanded phase is shown by a change in slope of the $\Pi$-A isotherm. This phase is characterized by coherent fluidity with a smaller density than the liquid condensed phase or a bulk liquid as well as any corresponding solid bulk or surface phases. The liquid condensed phase results from an area per molecule that is small enough to restrict position but still allow for free molecular rotation on the surface. The solid phase exists where molecules are highly ordered and packed as tightly together as possible. The limiting area per molecule permits no free movement within the dense, rigid film. At areas per molecule smaller than those responsible for the solid phase, film collapse is seen. In the collapse regime, molecules cease to maintain their ordered “two-dimensional” arrangement and begin to pile up on top of one another to eventually form multilayers. In the case of polymers, only the gaseous phase, a single liquid phase, and the collapse state have been observed in the $\Pi$-A isotherms.

The first materials studied as monolayers were olive oil and castor oil. These early experiments gave evidence to support an important theory about the spreading of oil on water. Both Rayleigh and Langmuir theorized that spreading was a function of the attraction of the hydrophilic portion of the oil molecule to the water versus the attraction of the hydrophobic portion to other oil molecules. During monolayer formation through spreading on water, the hydrophilic portion of the oil is solvated in the water without causing the hydrophobic portions to lose contact with each other. It can then be concluded that spreading is a result of the presence of some functional group on a molecule that has an affinity for the subphase. This being the case, the opposite must also be true. A molecule with no hydrophilic groups should not spread at all. Hardy showed this in 1912 through his studies of several saturated hydrocarbons, including paraffin oil, on water. Instead of spreading out across the surface, the oils formed visible lenses. Lens formation is also apparent when molecules with a hydrophilic group have formed a monolayer on the water surface. As more molecules are added there is no water surface left, only the hydrocarbons perpendicular to the surface. Therefore, the hydrophilic groups present in the additional molecules do not spread across the hydrocarbon surface that was formed by the first monolayer. The hydrocarbon tails are not always positioned perpendicular to the surface, however. If double bonds are present,
they too behave as if they were slightly hydrophilic groups. This perturbation of side-chain packing results in molecules that may be positioned horizontally or at some angle to the surface. As the amount of available area per molecule decreases, the stronger hydrophilic group displaces the weaker one, the double bond in this case, and a more perpendicular arrangement is eventually achieved. It is now important to discuss the Wilhelmy plate method by which surface pressure is measured.

Surface pressure ($\Pi$) is the conceptual inverse of surface tension ($\gamma$), which can be defined as the tendency of liquids to reduce their surface area. This value is represented quantitatively as

$$\Pi = \gamma_0 - \gamma$$  \hspace{1cm} (1-1)

where $\gamma_0$ is the surface tension of a pure liquid and $\gamma$ is the surface tension of a liquid covered with a monolayer. As the surface tension of a pure liquid drops with the addition of a surfactant, the surface pressure will similarly rise. Surface tension acts on the Wilhelmy plate in a downward direction, as does gravity. The water displacement of the plate itself and the subsequent buoyancy act in an upward direction (Figure 1.2). As the immersion depth of the plate is small, the buoyancy effect is generally neglected. Qualitatively, the forces on the plate are the weight of the plate minus the upward force from buoyancy plus the surface tension. Surface tension can be calculated by

$$\gamma = \frac{F_{\text{obs}} - w}{2(\ell + t)\cos\theta}$$  \hspace{1cm} (1-2)

with $F$ equal to the experimental force, $w$ being the weight of the plate, $\ell$ and $t$ being the length and thickness of the plate respectively, and $\theta$ representing the contact angle between the subphase and the plate. Once a monolayer is spread onto the subphase, surface pressure becomes a non-zero number. Recalling from equation (1-1) that surface pressure is the surface tension of the pure liquid minus the surface tension of the film-covered liquid it can be rewritten as
Figure 1.2 – Forces Acting on the Wilhelmy Plate

\[ F_{\text{obs}} \]

weight \( (w) \), surface tension \( (\gamma) \)
\[ \Pi = \frac{F_{\text{obs, pure}} - F_{\text{obs, film}}}{2(\ell + t)\cos\theta} \]  

(1-3)

If it is assumed that the contact angle is 0º and that the thickness of the plate is much smaller than the length, the above expression can be simplified to

\[ \Pi = \frac{F_{\text{obs, pure}} - F_{\text{obs, film}}}{2\ell}. \]  

(1-4)

The plate can be made of either chromatography paper or sand blasted platinum. Both are cleaned with chloroform and rinsed with ultra pure water prior to each use. It is apparent from the above equations that a dry plate will give a different surface pressure measurement than a wet plate so it is imperative that the plate be positioned in the subphase and be allowed to equilibrate before starting the experiment.

1.2 Thin Films

When operating at a constant surface pressure, films of suitable monolayers can be deposited onto solid substrates. For a monolayer to be deposited onto a substrate, there are two factors which must be considered. First, the monolayer must be hydrophobic enough to be largely insoluble in the water subphase. Second, the film must have enough rigidity to remain ordered on the surface but must also have a low enough viscosity to transfer to the substrate without cracking. If polymer chains are too swollen with water, the monolayer will not be ordered enough to produce a uniform LB film. Film deposition can occur in one of three patterns: x-type, y-type, or z-type (Figure 1.3). Films thought to be deposited by x-type or z-type are sometimes shown to actually be y-type after x-ray analysis. The deposition type can also switch at some point during the deposition. 10 All of these types involve the transfer of an amphiphilic molecule from the subphase surface to the substrate surface via the dipping of the substrate through a compressed monolayer. This process allows surface behavior at the gas/solid interface to be studied. The major advantage of making films in this way is that each layer is deposited individually and is exactly one molecule thick. It follows, then, that the number of molecular layers can be predetermined and highly ordered films of controlled thickness can be obtained.

The surface pressure at which these films are transferred is important because of the arrangement of molecules on the subphase surface at different pressures. The most
Figure 1.3 – Film Deposition Types

X-Type

Y-Type

Z-Type
desirable transfer occurs from the liquid condensed phase when the film has been compressed as densely as possible without collapsing into multilayers. A collapsed film or a film in which the molecules are loosely packed together will not produce uniform films on the surface of the solid substrate. Abnormal film adhesion can also lead to poor transfer in areas where the film is being deposited and removed repeatedly. Poor adhesion can be caused by a number of factors with the major one being a contaminated substrate. Sources of substrate contamination are varied so any cleaning procedures used prior to deposition must be carried out very carefully and thoroughly in the cleanest possible environment. The quality of the deposited film can be measure quantitatively through the transfer ratio (TR) given by

\[ TR = \frac{\text{area of monolayer removed from subphase at constant pressure}}{\text{area of substrate immersed in water}} \]  

LB films were originally made with amphiphilic molecules although the technique is not limited to this class of materials. While small amphiphilic molecules are easily deposited, the resulting films tend to experience thermal and mechanical stability problems that make them unsuitable for many technological applications. Another problem is that the hydrophobic "tails" of these amphiphiles generally needed to be at least fourteen carbons long to result in a uniform film, which limits the minimum film thickness. In response to these issues, thin films of polymers were made and shown to have improved stability. In fact, heating films of poly(octadecene-1/maleic anhydride) copolymers actually showed reduction in conductive defects as irregularities in the films caused by an electrode were "baked" out at 293K. It is important to note that polymers used in this application generally have alternating hydrophilic and hydrophobic groups along the entire length of the chain rather than having one endgroup with a hydrophobic functionality and the other end with a hydrophilic functionality.

Two main methods of creating polymer thin films by LB can be found in the literature. The first method involves the deposition of the vinyl amphiphiles followed by solid-state photopolymerization. The second method is the deposition of preformed polymers. In this case, the polymer is synthesized and then dissolved in a volatile solvent. The solution is spread on the surface and deposited onto the substrate after the solvent has evaporated according to the procedures discussed above. The problem with
the first method is that the intermolecular distance decreases during the polymerization so cracks in the film are common. The LB deposition of preformed polymers is therefore more likely to result in homogeneous films. While LB is the only method used in this thesis, there are other ways to deposit polymer films onto solid substrates such as the spincoating and Langmuir-Schaeffer (LS) processes.

Spincoating employs centrifugal forces to sweep the deposited polymer solution across the wafer in a uniform fashion. While effective at creating thin layers and useful for almost all polymers, uniformity is often a problem due to the large number of factors involved including solution concentration, solvent, spin speed, acceleration rate, spin time, and deceleration. In addition, the rheology of the spun solution must be considered. A liquid with a high viscosity requires more force to induce flow across the surface of the substrate. As viscosity increases, the film coverage decreases until no flow occurs at a constant spin speed. As with LB, spincoating requires wetting of the substrate by the liquid to achieve appropriate film formation and is affected by the same contamination issues. The thickness of films made by spincoating is dictated by centrifugal force. As a result, uniform thickness over the entire substrate is difficult to achieve unlike with LB where uniform thickness is a major advantage. LB can also result in oriented materials unlike spincoating.

Langmuir-Scheaffer (LS) film formation occurs in much the same way as LB except that the substrate is dipped in and out of the monolayer in a horizontal, rather than vertical, manner. The LS method has an advantage over the LB method because the films made are from monolayers compressed into the solid phase. Molecules without a liquid condensed phase cannot be transferred using LB but can be transferred as rigid films using LS. The disadvantage of LS is that currently only a monolayer or bilayer can be deposited. Multilayers are impossible due to the horizontal transfer mechanism.

1.3 Interfacial Tension and the Critical Micelle Concentration

Interfacial (surface) tension ($\gamma$) is the force per unit length acting on a surface. As discussed above, the interfacial tension of a surfactant solution, written as

$$\gamma = \gamma^0 - \Pi$$

is decreased by increased surface pressure. Rearranging equation (1-6) we arrive again at the equation for surface pressure ($\Pi$), (1-1). As the concentration of a surfactant in
solution increases, more is present at the surface causing a decrease in interfacial tension and an increase in surface pressure. The formation of micelles occurs above a specific surfactant concentration and is defined as "the concentration of surfactants in solution above which the development of micelles causes variation in chemical and physical properties of the solution." These variant properties include not only interfacial tension but also turbidity, osmotic pressure, and conductivity of the solution. This concentration, the critical micelle concentration (c.m.c.), can be determined in a number of ways, most notably by molar conductivity, tensiometry, and light scattering which will be discussed in more detail in a subsequent chapter.

During a conductivity experiment, the transport of charged species is monitored and events that occur in the solution can then be determined. Predictions can also be made about non-charged molecules. The conductivity of a solution is directly related to the number of ions present. Molar conductivity ($\Lambda_m$) varies with solution concentration and is measured in an electrolyte solution by a resistance bridge with a conductivity cell in one arm. The quantity is written as

$$\Lambda_m = \frac{\kappa}{c}$$

with $\kappa$ being the conductivity and $c$ equaling the molar concentration of solution. The dependence on concentration is derived from the fact that, in practice, the conductivity is not proportional to solution concentration. Therefore, as the c.m.c. is reached, the conductivity of the solution will change and the formation of micelles can be illustrated on a plot of $\Lambda_m$ (S•cm²•mol⁻¹) versus $c$ (mol•L⁻¹).

Tensiometers measure the surface tension of liquids using a force balance to which a Wilhelmy plate is attached. Surface tension measurements can then be made as a function of surfactant concentration in solution. As micelles form, the amount of surfactant at the surface decreases thereby decreasing the surface tension of the solution. This decrease is visible on a plot of surface tension (mN/m) versus solution concentration (g/L). The critical micelle concentration can then be determined from these plots. It is important to note that there are three unknowns involved in any tensiometry experiment: the perimeter of the plate, the contact angle between the plate and the subphase, and the surface tension. Since the perimeter of the plate can be calculated, and the contact angle
is assumed to be equal to zero, the surface tension can then be measured. Paper plates have an advantage over platinum plates in terms of the contact angle. The subphase can soak into the paper plate ensuring that the contact angle is zero. This soaking process takes a finite time and must be completed before any measurements are taken to guarantee accurate surface tension readings.

1.4 Brewster Angle Microscopy

There are several methods of surface imaging that are compatible with Langmuir and Langmuir-Blodgett films including fluorescence microscopy, atomic force microscopy (AFM), and Brewster angle microscopy (BAM). The advantage of BAM is that a Langmuir film can be studied \textit{in situ} without further chemical perturbation or the deposition of the film onto a solid substrate. Another advantage is that the angle of incidence is not perpendicular to the surface as with other methods. Since the reflectivity about Brewster's angle is associated with the angle of incidence and the angle of refraction, $\theta_0$ and $\theta_1$ respectively, the theory behind this technique can be related simply to Snell's Law written as

\[ n_0 \sin \theta_0 = n_1 \sin \theta_1. \] (1-8)

To define Brewster's angle ($\theta_b$), $\tan \theta_b = n_1 / n_0$, it is important to note that light passing through a medium with a lower refractive index ($n_0$) into a medium with a higher refractive index ($n_1$) will generally reflect p-polarized light. However, when operating a microscope at Brewster's Angle, no p-polarized light will be reflected by a pure water surface. The addition of a film to the surface introduces some reflectivity that is dependent upon the film’s thickness and the refractive index (Figure 1.4). The reflection caused by the monolayer will increase in brightness as film thickness and film index increase.\textsuperscript{2}
Figure 1.4 – Brewster Angle Microscopy (BAM) Beam Diagram

Brewster's Law

\[
\tan \theta_b = \frac{n_{\text{water}}}{n_{\text{air}}}
\]

---

Arrows indicate radiation polarized in the \( p \) direction
A typical BAM instrument consists of a source, a polarizer with the field polarized parallel to the plane of reflection, and a detector. The polarizer serves to filter out all light parallel to the direction of the incident beam except one. The polarizer can be placed either in the path of the incident beam to polarize all the radiation in the $p$ direction before it contacts the surface, as in traditional BAM, or it can be placed in the path of the reflected beam to filter out any residual $s$ component before the reflected $p$ radiation reaches the detector, as in Mini-BAM. By placing the polarizer in the path of the reflected beam, better resolution is achieved (Figure 1.5). Fluorescence labeling can also be employed to further understand the phase behavior of Langmuir films. By labeling one of the components of a two-component film, fluorescence microscopy can be used to concretely identify the phases observed with BAM.
Figure 1.5 – Traditional vs. Mini-BAM: The Effect of Polarizer Position

a. Traditional BAM

b. Mini-BAM
CHAPTER 2
Experimental Methods

2.1 Langmuir-Blodgettry

The experiments presented were done on one of two instruments, a KSV 5000 single trough or a NIMA 601BAM equipped with a Brewster angle microscope. Both troughs are constructed of Teflon® that serves as a hydrophobic surface that can be aggressively cleaned without degradation. This hydrophobicity allowed the water subphase to be poured to a distance of approximately 1 mm above the top edge of the trough for all experiments. The barriers, made of either the hydrophilic acetal resin polymer Delrin® or hydrophobic Teflon®, were then able to efficiently sweep the water surface prior to and during the molecular compression of the surface (Figure 2.1). Complete coverage of the subphase surface by the barriers as they move was necessary to remove any dust or other contaminants from the surface prior to spreading. A clean subphase surface was achieved by moving the barriers toward each other thereby pushing contaminants into the center of the trough where they were suctioned away with the aid of a vacuum pump. This method also kept all spread molecules in the area between the barriers during the experiments.

The trough and Teflon® barriers were cleaned with chloroform while the Delrin® barriers were cleaned with isopropanol. The water used to fill the trough had fewer than 5 parts per billion organics (Milli-Q Gradient A-10). The instruments are housed in Plexiglas® boxes to maintain humid environments that are as dust free as possible. The KSV instrument is housed on a vibration isolated table (Kinetic Systems, Vibraplane) in a portable clean room fitted with four HEPA filters (CRI). The NIMA instrument is maintained on an optical table with black curtains on all sides to minimize stray light and improve BAM performance (Newport RS-2000). The four laminar flow isolator table legs provide vibration isolation (Newport I-2000 series).

The systems each measured surface pressure with a force balance to which a Wilhelmy plate was attached. Platinum plates were used with the KSV instrument and paper plates were used with the NIMA instrument. After cleaning the subphase, a predetermined volume of solution (based on solution concentration and desired initial area per molecule) was spread using a micro syringe (Hamilton). According to the procedure
Figure 2.1 – Langmuir-Blodgett Trough Schematic

Temperature Controlled Teflon® Trough

force balance

barrier

Wilhelmy plate

barrier

aqueous subphase
first developed by Pockels $^{22}$, the spread material was allowed to remain on the surface for up to fifteen minutes. This equilibration time permitted the volatile solvent to evaporate thereby leaving only the desired molecules on the surface. Temperature was controlled using a circulating bath (Neslab RTE-111). A computer controlled interface unit translated the barriers and dipper position, and acquired the subphase temperature from a thermocouple.

2.2 Compression Isotherms

Surface pressure data can be recorded over a wide range of molecular areas using a compression isotherm. During this type of experiment, barriers were compressed at a specific rate as the spread molecules went through phase transitions up through and beyond the collapse of the Langmuir film. This type of experiment was used to determine the area a molecule occupied as the film went through specific phase transitions. This experiment was also especially useful for determining the phase behavior of polymer blends at A/W. In this case, varying concentrations of POSS were dissolved in chloroform along with poly(dimethylsiloxane) (PDMS) or poly(vinylacetate) (PVAc). The mixing characteristics of the blends were determined by comparing the mixed solution $\Pi$-A compression isotherms with those of the individual components. A mixed isotherm in between those of the individual components suggested potential compatibility. Hence, the isotherms were used to speculate about the surface behavior and make predictions about morphology for verification by Brewster angle microscopy (BAM) experiments.

2.3 Quasistatic Isotherm Compression-Relaxation Experiments

While experimentally similar to a compression isotherm, the quasistatic isotherm allows time for pressure relaxation after compression of a Langmuir film. Reducing the area available on the surface by a controlled amount and then holding the barriers in position for a set time interval provides information about the stability of a given monolayer state. Compressing quasistatically is useful for determining film stability both above and below the collapse pressure. If a condensed film is stable, there is increased potential for making Langmuir-Blodgett thin films from that material.
2.4 Interfacial Tension Measurements

Interfacial (surface) tension ($\gamma$) was measured using the same force balance/Wilhelmy plate setup as described above. For the experiments discussed, a temperature-controlled glass water jacket was used for the solution container while the balance was dipped in and out of the liquid sample to take measurements. The system was enclosed in a small Plexiglas® box with the balance and the water jacket inside. The doors to the box can be closed and beakers of solvent added to maintain a saturated environment during the measurements. The polymer solvent for all interfacial tension measurements presented was toluene, which was also used as a reference solution. Measurements were taken starting with the solution of lowest surfactant concentration and concluding with the most concentrated solution. The plate was placed in contact with the solution and after allowing for equilibration with the solution, a period of about five minutes, it was removed and the balance zeroed. The plate was then quickly put back in the solution to prevent drying and a measurement was recorded. This procedure was used for both the poly(dimethylsiloxane-b-(3-cyanopropyl)methylsiloxane-b-dimethylsiloxane) (PDMS-PCPMS-PDMS) triblock and the poly(dimethylsiloxane-2-ethyl-2-oxazoline) (PDMS-PEtOx) diblock copolymers.

2.5 Film Deposition

Films were deposited onto solid substrates using the KSV 5000 single trough instrument. The subphase bath contains a well in the center that is 87 millimeters deep and 118 millimeters long and 37 millimeters wide. The substrate was attached to an electronic dipper positioned above the well. Substrates used in the experiments discussed were silicon wafers that were cleaned and hydrophobized prior to use. The 0.1 mm thick, 10 cm diameter wafers were first cut into smaller rectangular pieces using a diamond tipped cutter. The pieces were then immersed in 99.9% HPLC grade dichloromethane, covered, and sonicated (Fisher Scientific FS140H) at room temperature for fifteen minutes. After being dried with nitrogen, the wafers were each put in a solution of 1:1:5 concentrated ammonium hydroxide, 30% hydrogen peroxide, and ultra pure water respectively, and heated for roughly one hour or until most of the ammonia had boiled away. The now hydrophilic wafers were thoroughly rinsed with the ultra pure water and dried with nitrogen. The dry pieces were placed in a glass dome with a few
drops of hexamethyldisilazane (HMDS) and put in an oven (Lindberg/Blue V0914A) at 80º C for as little as four and as many as 168 hours. Film deposition was monitored at constant pressure by recording the transfer ratio (equation 1-5) onto the now hydrophobic wafers. Ideally, the transfer ratio would be equal to one for each deposited layer because in that case the amount of material removed from the trough would be exactly equal to the amount added to the substrate. A transfer ratio of greater than one or far less than one indicates poor or negligible transfer that could be a result of a dirty substrate, an unstable monolayer, or a molecule that is unsuitable for LB transfer.

2.6 Brewster Angle Microscopy

The microscope used consists of a 688 nm laser source, two filters (one for polarizing the light initially and one for selecting out the polarization of the reflected light), and a detector. When imaging Langmuir films, a black plate was placed in the bottom of the subphase bath to minimize scattering from the refracted light by the white Teflon® surface. The source beam was projected onto the surface above the plate through the monolayer and reflected out to the detector window. The image was viewed on a black and white monitor (Phillips). Image data was acquired by a computer equipped with an appropriate video card (Accurion) and National Instruments IMAQ® imaging software.

2.7 Materials and Characterization

Professor Judy Riffle's group in the chemistry department at Virginia Tech synthesized a family of triblock PDMS-PCPMS-PDMS copolymers by first synthesizing the PCPMS oligomers from a bulk equilibration of 1,3,5,7-tetra(3-cyanopropyl)-1,3,5,7-tetramehtylcyclotetrasiloxane (D₄CN) (Gelest) with lithium hydroxide as the initiator at 140ºC (Figure 2.2). By varying the ratio of D₄CN to initiator, the block molecular weight could be controlled. The PDMS blocks of varying molecular weights were then synthesized by adding hexamethyldicyclotrisiloxane (D₃) (Gelest) and dichloromethane to the reaction flask with tetrahydrofuran (THF) as the reaction promoter. The chains were terminated with excess trimethylchlorosilane and their formation was monitored via ¹H NMR and GPC.²³ All solvents were HPLC grade.

Professor Riffle's group also synthesized a poly(dimethylsiloxane-2-ethyl-2-oxazoline) diblock copolymer by first anionically synthesizing the PDMS prepolymer
using hexamethylcyclotrisiloxane (D₃) as the monomer and sec-butyl lithium as the initiator. Anhydrous tetrahydrofuran (THF) was the propagation solvent and the chains were terminated using benzyl chloride. The monofunctional PDMS was then combined with the ethyl-oxazoline monomers in the presence of chlorobenzene and thermally propagated. The chains were then precipitated into methanol (Figure 2.3). The reactions were monitored via $^1$H NMR. All solvents were HPLC grade. Professor Riffle's group also synthesized a 2K sample of poly(dimethylsiloxane) (PDMS) via living anionic polymerization. The chains were initiated with sec-butyl lithium and terminated with a trimethylsilyl group. The polymer was soluble in chloroform which was used as the spreading solvent. Molecular weight was determined by gel permeation chromatography (GPC).

The poly(vinylacetate) (PVAc) sample used was prepared by Dr. Woongki Lee at the University of Wisconsin, Madison. The polymer had a viscosity average molecular weight of 1,280K and was soluble in chloroform which was used as the spreading solvent. The polyhedral oligomeric silsesquioxane (POSS) derivatives were synthesized at Air Force Research Lab, California and provided by Dr. Brent Viers. The POSS molecules were synthesized through the hydrolysis of either a trichlorosilane or a trialkoxysilane. The PDMS/POSS copolymers were synthesized according to a general procedure published by Lichtenhan in 1993 using PDMS oligomers and various POSS monomers. The POSS samples were soluble in chloroform which was used as the spreading solvent.

The poly(1-alkene-alt-maleic anhydride) (PXcMA) polymers were provided by Dr. Calvin Verbrugge of S.C. Johnson & Son, Wisconsin and used in their hydrolyzed form on a subphase of 0.01M HCl. The 1-hexene, 1-octene, and 1-decene derivatives were dissolved in 1:1 solutions of anhydrous THF and dichloromethane which was used as the spreading solvent. The 1-octadecene derivative was dissolved in a 3:1 solution of anhydrous diethyl ether and hexane which was used as the spreading solvent. The THF and diethyl ether were each dried over sodium metal in the presence of benzophenone. The polymer molecular weights were 34K, 18K, 30K, 320K, and 128K form 1-hexene to 1-octadecene, respectively, with polydispersity indices (PDI=\(M_w/M_n\) of 4.2, 2.6, 3.4,
15.5, and 2.91 respectively. Molecular weights and PDI values were determined by GPC by Dr. Thomas Mourey of Eastman Kodak.
Figure 2.2 – Synthetic Scheme for PDMS-PCPMS-PDMS Triblock Copolymers

\[ \text{Figure 2.2 - Synthetic Scheme for PDMS-PCPMS-PDMS Triblock Copolymers} \]
Figure 2.3 – Synthetic Scheme for PDMS-PETOx Diblock Copolymer

1. 45% in cyclohexane
   room temp.
2. 10 vol. % THF

1. 110°C 40-60 hours
2. KOH in MeOH
   room temperature
CHAPTER 3

Interfacial Tension and Critical Micelle Concentration Determinations of Poly(dimethylsiloxane-b-(3-cyanopropyl)methylsiloxane-b-dimethylsiloxane) Triblock Copolymers (PDMS-PCPMS-PDMS) and Poly(dimethylsiloxane-b-2-ethyl-2-oxazoline) (PDMS-PEtOx) Diblock Copolymers

3.1 Tensiometry Results

The members of the poly(dimethylsiloxane-b-(3-cyanopropyl)methylsiloxane-b-dimethylsiloxane) (PDMS-PCPMS-PDMS) series of block copolymers (Figure 2.4) are useful stabilizers for cobalt particles in magnetic fluids. These fluids are synthesized by reducing the metal inside a polymeric micelle and then dispersing the encapsulated particles in a carrier fluid (Figure 3.1). They have been found to exhibit microphase separation using differential scanning calorimetry (DSC) where the PDMS blocks have $T_g$'s of $-118^\circ$C and the PCPMS block has a $T_g$ of $-65^\circ$C in the second heating scan (Figure 3.2).

Magnetic fluids are useful both industrially and medically in applications such as rotating shaft seals and loud speaker coils as well as magnetic resonance imaging (MRI) contrast agents. Magnetic fluids synthesized using PDMS-PCPMS-PDMS block copolymers can potentially act as repair agents for retinal damage. If the retina is torn, fluid can leak out of the tear into the space behind the retina and cause it to detach resulting in vision loss. In order to repair the detachment, it has been proposed that a magnetic scleral buckle be attached to the eye. A magnetic fluid introduced into the retina will then be attracted to the buckle and hold the detached piece in place. Thus, the determination of the critical micelle concentration (c.m.c) of these polymers is very important in developing a method for synthesizing and controlling the size distribution of superparamagnetic nanoparticle dispersions. Superparamagnetism results from a dispersion in which each particle acts as one magnetic domain. When an external magnetic field is applied, all the domains orient in the same direction. When the external field is removed, the domains return to a statistically random orientation. Superparamagnetism is characterized by a lack of hysteresis in this process. If some of the domains remain oriented after the removal of the external field, the dispersion is said to be ferromagnetic. For the particles discussed here, a size of 10 nm is critical for
PDMS-PCPMS-PDMS forms micelles above the c.m.c. It can then be reacted with cobalt octacarbonyl in the presence of toluene to form cobalt nanoparticles. Each nanoparticle has about 47,600 cobalt atoms and about 46 polymer chains (particle size determined by TEM). The nanoparticles can then be dispersed in a PDMS carrier fluid and the toluene is evaporated.
Figure 3.2 – Differential Scanning Calorimetry (DSC) Trace for a PDMS-PCPMS-PDMS Triblock Copolymer \textsuperscript{23}
superparamagnetism. The size of the cobalt nanoparticles was determined using dynamic light scattering (DLS).

Toluene was used as the solvent for all interfacial tension measurements because it is a good solvent for the PDMS blocks but a poor solvent for the PCPMS block. Micelle formation is thereby encouraged as the PCPMS block reduces its surface area to minimize contact with the bulk solvent while the PDMS blocks remain solvated and swollen resulting in structures with a PCPMS core and a PDMS corona (Figure 3.3). In order to determine the c.m.c., the interfacial tension was measured as a function of block molecular weight over a range of surfactant concentrations. As the surfactant is added to the solution, the interfacial tension decreases (Figure 3.4). At the critical micelle concentration (c.m.c.), additional increases in the bulk surfactant concentration produce no further decreases in surface tension. The plot shows that the c.m.c. consistently lies between about 0.01 g/L and 0.1 g/L. Polymer molecular weight does not seem to significantly alter the c.m.c. in the case of this triblock series although the interfacial tensions are consistently lower as the molecular weight of the PCPMS block increases for a fixed block length. The molecular weight of the PDMS blocks does not appear to affect the interfacial tension in as predictable a manner due to the influence of the PCPMS block. For a fixed PCPMS block length, the larger PDMS block shows a larger interfacial tension (γ) value as toluene is a good solvent for PDMS. Hence a plot of γ vs. bulk concentration (C) shows a precipitous drop from the pure liquid surface tension value to a plateau of constant interfacial tension. The crossover from decreasing to constant interfacial tension is taken as an estimate of the c.m.c. Dynamic light scattering shows that increased molecular weight of the PCPMS block results in aggregated micelles due to the insolubility of the PCPMS in toluene. It is useful to calculate the surface excess (Γ) for all the concentrations studied to better illustrate what is happening in the solution at the c.m.c. The surface excess can be obtained from the expression for the Gibbs adsorption isotherm written as

\[ \Gamma = -\frac{c}{RT} \frac{\partial \gamma}{\partial c} \]  

(3-1)

where \( c \) is concentration, \( R \) is the gas constant, \( T \) is temperature in Kelvin, and \( \gamma \) is the interfacial tension. At \( C_{\text{bulk}}=1 \times 10^{-4} \text{ g}\cdot\text{L}^{-1} \), well below the c.m.c., the surface excess is
The PCPMS central blocks move to the surface because they are insoluble in toluene. As the concentration of surfactant in solution increases, the surface becomes more populated with polymer chains. At the c.m.c., the polymer chains form micelles and there is an equilibrium between free chains and micelles.
Figure 3.4 – Interfacial Tensions of PDMS-PCPMS-PDMS Triblock Copolymer Solutions as a Function of Block Molecular Weight in Toluene at 22°C
on the order of $2 \times 10^{-8}$ mol$\cdot$m$^{-2}$. A 50% increase would give a value of $3 \times 10^{-8}$ mol$\cdot$m$^{-2}$ which, if divided by $2 \times 10^{-8}$ mol$\cdot$m$^{-2}$ would give 0.5. As the solution concentration approaches the c.m.c., the surface excess concentration is now about twice as large at $4 \times 10^{-8}$ mol$\cdot$m$^{-2}$. In this case, the toluene insoluble PCPMS blocks are moving to the surface. As the surfactant concentration in solution reaches the c.m.c., the surface excess concentration will remain constant as an equilibrium between micelles and free surfactant in solution is established.

Preliminary interfacial tension measurements of an alternative system for synthesizing and controlling magnetic nanoparticle dispersions, a diblock poly(dimethylsiloxane-2-ethyl-2-oxazoline) (PDMS-PetOx) copolymer system (Figure 2.5), yielded similar but more erratic data (Figure 3.5). However, there is still a distinct change in slope between 0.0001 to 0.001 g/L. Again, calculations of surface excess at solution concentrations at and around the c.m.c. help to describe micellar formation. For this system at $C_{\text{bulk}} = 1 \times 10^{-4}$ g$\cdot$L$^{-1}$, below the c.m.c., the surface excess is approximately equal to $6 \times 10^{-8}$ mol$\cdot$m$^{-2}$. At concentrations approaching the c.m.c., the surface excess triples to about $2 \times 10^{-7}$ mol$\cdot$m$^{-2}$.

3.2 Dynamic Light Scattering Results

Dynamic light scattering is based on the time dependence of scattered light from a region of a solution and is another way of determining the c.m.c. The changes in the intensity of the scattered light, measured by a detector, are related to the diffusion coefficients of species through a solution. Diffusion coefficients can then be related to particle size through theoretical calculations based on Doppler shifts caused by Brownian motion. The hydrodynamic radius ($R_h$), or Stokes radius, of a particle can then be determined based on a theoretical hard sphere with the same diffusion coefficient. The equation used to calculate $R_h$ using the diffusion coefficient is the Stokes-Einstein equation and is written as

$$D = \frac{kT}{6\pi\eta R_h} \tag{3-1}$$

where $k$ is the Boltzmann constant, $T$ is the temperature, $\eta$ is the solvent viscosity, and $D$ is the diffusion coefficient. The denominator is merely the friction coefficient for a sphere.
in a viscous medium. These calculations can be problematic, however, because the spheres on which they are based do not exist. Therefore, the calculated radius is only
Figure 3.5 – Interfacial Tensions of PDMS-PEtOx Diblock Copolymer Solutions in Toluene at 22°C

*Trendline
indicative of the apparent size of the solvated dynamic structure, resulting in the term "hydrodynamic radius". Still, the measurement of $R_h$ values of particles in solution is a convenient way to determine the formation of micelles. An abrupt increase in $R_h$ would denote aggregation or micellar behavior.

In the case of the two PDMS-PCPMS-PDMS triblock copolymers with low molecular weight PDMS blocks, the $R_h$ value sharply increased for solutions between 0.001 and 0.01 g/L which means that larger structures are abruptly forming and that the c.m.c. was within the range estimated by the aforementioned interfacial tension measurements (Table 3.6a). The increase in molecular weight of the PDMS block resulted in an increased $R_h$ value between 0.01 and 0.1 g•L$^{-1}$ for the 15K-2K-15K copolymer and 0.1 and 0.5 g•L$^{-1}$ for the 15K-5K-15K copolymer (Table 3.6b). This makes intuitive sense due to the solubility of the PDMS in toluene.

As a result of c.m.c. determination by tensiometry and dynamic light scattering, the cobalt dispersions were synthesized at a concentration that was several orders of magnitude above the c.m.c. to ensure the existence of the PDMS-PCPMS-PDMS micelles.

3.3 Temperature Dependence

An additional feature of the nanoparticle synthesis is the use of elevated temperatures for the reduction of cobalt carbonyl at a temperature of 45ºC. One possible concern is that measurements of the c.m.c. near room temperature are invalid at elevated temperatures. Literature studies show the c.m.c. is not terribly sensitive to temperature for polymeric surfactants$^{26}$ In order to test the temperature dependence of the PDMS-PCPMS-PDMS system, the interfacial tensions of 15K-5K-15K triblock copolymer (the highest total molecular weight polymer) solutions as a function of temperature were made. Figure 3.7 shows a well-defined trend. The temperature range was chosen based on the reaction temperatures used to make the cobalt dispersions. Temperatures from 25ºC to 45ºC were studied. As temperature increased, the interfacial tension decreased over the full range of concentrations studied. This trend is important for this system because it shows that the micelles are still present once the reaction temperature reaches 45ºC. Moreover, the c.m.c. for this system is temperature insensitive over the range considered.
Table 3.6 – Dynamic Light Scattering (DLS) Data for PDMS-PCPMS-PDMS Triblock Copolymer Solutions in Toluene\textsuperscript{23}

<table>
<thead>
<tr>
<th>Concentration (g•L\textsuperscript{-1})</th>
<th>5K-2K-5K</th>
<th>5K-5K-5K</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>15.35 +/- 0.08 nm</td>
<td>21.35 +/- 0.61 nm</td>
</tr>
<tr>
<td>1</td>
<td>13.54 +/- 0.35 nm</td>
<td>20.43 +/- 0.06 nm</td>
</tr>
<tr>
<td>0.5</td>
<td>12.80 +/- 0.16 nm</td>
<td>18.61 +/- 0.09 nm</td>
</tr>
<tr>
<td>0.1</td>
<td>12.02 +/- 1.11 nm</td>
<td>15.45 +/- 2.28 nm</td>
</tr>
<tr>
<td>0.01</td>
<td>11.47 +/- 0.61 nm</td>
<td>12.19 +/- 0.86 nm</td>
</tr>
<tr>
<td>0.001</td>
<td>3.38 +/- 1.50 nm</td>
<td>4.13 +/- 1.03 nm</td>
</tr>
</tbody>
</table>

a. Lower molecular weight polymers

<table>
<thead>
<tr>
<th>Concentration (g•L\textsuperscript{-1})</th>
<th>15K-2K-15K</th>
<th>15K-5K-15K</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>11.78 +/- 0.62 nm</td>
<td>26.70 +/- 0.08 nm</td>
</tr>
<tr>
<td>1</td>
<td>11.63 +/- 0.73 nm</td>
<td>21.77 +/- 0.02 nm</td>
</tr>
<tr>
<td>0.5</td>
<td>11.86 +/- 0.49 nm</td>
<td>21.33 +/- 0.15 nm</td>
</tr>
<tr>
<td>0.1</td>
<td>11.72 +/- 0.65 nm</td>
<td>6.99 +/- 0.14 nm</td>
</tr>
<tr>
<td>0.01</td>
<td>2.8 +/- 0.40 nm</td>
<td>5.25 +/- 0.038 nm</td>
</tr>
<tr>
<td>0.001</td>
<td>N/A</td>
<td>4.38 +/- 0.05 nm</td>
</tr>
</tbody>
</table>

b. Higher molecular weight polymers
Figure 3.7 – Interfacial Tensions of 15K-5K-15K PDMS-PCPMS-PDMS Triblock Copolymer Solutions as a Function of Temperature in Toluene.
CHAPTER 4

Polyhedral Oligomeric Silsesquioxane Derivatives (POSS)

4.1 Pure Polyhedral Oligomeric Silsesquioxane (POSS) Behavior at Air/Water (A/W)

POSS molecules (RSiO$_{3/2}$, where R is an alkyl group) are organic/inorganic hybrids that are about 1-2nm in size. They can be functionalized in a variety of ways and exist as two main derivatives, the fully functional octasubstituted-POSS and the heptasubstituted trisilanol-POSS (Figure 4.1). These two principle derivatives are the products of a hydrolysis of trichlorosilanes or trialkoxysilanes. The octasubstituted POSS can be hydrolyzed to form the heptasubstituted derivative at any time although it is stable at room temperature in an environment with relatively high humidity (~70%).

By changing the functional groups (R) on a POSS molecule, the characteristics and surface activity can be changed. Possible functional groups include almost any organic group such as methyl, isobutyl, cyclopentyl, or cyclohexyl. Vinyl functional groups are also available which allow for the copolymerization of POSS with other monomers. This variety in functionalization is the source of one of the main differences between POSS molecules and customary fillers. Traditional organoclays (>10 nm) and inorganic fillers (>1 µm) are characteristically inert and have no direct interaction with the polymers they fill. However, some can be modified covalently to promote interactions. The opposite is true of POSS. POSS molecules with alkene functional groups are readily available and able to directly bond with the polymer matrix covalently. Other functional groups can be added as well and result in specific and non-specific interactions. Covalent POSS attachment results in polymers with higher glass transition temperatures ($T_g$) as well as increased hardness, toughness, fire retardance, and corrosion inhibition. POSS derivatives usually exist as temperature stable low density powders or oils which are biocompatible. They have high oxygen permeability and can be recycled.

By covalently incorporating POSS into poly(dimethylsiloxane) (PDMS), different properties like variable glass transition temperature ($T_g$) values have been achieved. By nature, POSS networks are very brittle but the addition of homogenously distributed PDMS segments has been shown to increase the fracture toughness of the networks along
Figure 4.1 – General Polyhedral Oligomeric Silsesquioxane (POSS) Structures

a. Octasubstituted POSS – "closed cage" structure

b. Heptasubstituted POSS – "open cage" structure
POSS polymers for spin-on glass applications are generally ladders with good oxidative stability, electrical insulation properties, and selective gas permeability that may allow them to be used as sensors. Other polymer architectures such as grafts and beads are also available (see Figure 4.17 for examples).

The octasubstituted and heptasubstituted molecules are similar in size and density but have very different behavior at A/W (Figure 4.2). The cross-sectional area of a molecule at the surface can be determined by extrapolating the linear portion of the \( \Pi-A \) curve through the abscissa. Using this method, the cross-sectional area of a molecule of heptasubstituted trisilanol-POSS derivatives are between 175 and 200 Å\(^2\). This value is in good agreement with the known size of the molecule (1-2 nm) and its bulk density. However, cross-sectional area estimates with the octasubstituted POSS, appear to be approximately one third to one fourth of the trisilanol's size, or approximately 30 to 50 Å\(^2\). Recalling that these two derivatives are about the same size and density, the films formed by the octasubstituted POSS must then be approximately three to four times thicker than those of the trisilanol POSS. This discrepancy can be explained by the differences in functional groups present on these molecules. The trisilanol POSS has three hydroxyl groups in one corner of the cube-like core. This structural feature would contribute to stronger interactions with the water subphase. Conversely, the octasubstituted molecule lacks strong hydrophilic groups and has no particular affinity for the water subphase. As a result, the trisilanol POSS is more likely to stay on the surface as long as possible until lateral pressure arising from compression becomes great enough to force the molecules away from the interface (collapse). Two outcomes seem possible for the octasubstituted POSS molecules. The first is that the molecules would continue to pile up in a vertical fashion indefinitely. Upon further inspection, this is unlikely because after about three to four layers, the domains would become too thick and heavy for the molecules to collapse vertically and also they must start to aggregate horizontally. As a result of weaker interactions with the subphase than the trisilanol molecules, the octasubstituted POSS molecules aggregate more readily such that smaller areas per molecule are observed at the onset of a liquid condensed phase.
Figure 4.2 – Π-A Isotherms of Octa- and Heptasubstituted POSS

![Graph showing Π-A Isotherms of Octa- and Heptasubstituted POSS](image)

- Cyclopentyl
- Isobutyl
- Cyclohexyl
- Cyclohexyl Trisilanol
- Cyclopentyl Trisilanol
- Isobutyl Trisilanol
An additional functional group effect can be seen in the case of the trisilanol POSS. The size and hydrophobicity of the R groups changes the collapse pressure of the trisilanol films. As the groups get more bulky and more hydrophobic, the interactions between the subphase and the hydroxyl groups on the trisilanol cage begin to weaken. In essence, the big groups are pulling the hydrophilic corner of the molecule off of the surface thereby decreasing the collapse pressure. The clear trend seen on the plot is a function of the strength of the interaction between the water and the hydroxyl groups. If they were groups having a stronger interaction with water, such as carboxylic acids, the functional group effect would probably be less pronounced. Since the octasubstituted POSS does not have the affinity for the subphase that the trisilanol does, the effect of R group size and hydrophobicity does not have the same result. In fact, no trend is apparent so it can be assumed that the type of R group present on the octasubstituted POSS has very little effect on its behavior at A/W. However, the group present could still have a substantial affect on how an octasubstituted POSS nanofiller interacts with a polymer matrix at A/W.

BAM images of the films of the octasubstituted isobutyl-POSS are very different from those of the trisilanol isobutyl-POSS, which is an expected result based on the behaviors described above. The images of the octasubstituted POSS show very large domains, even at low surface pressures and large areas per molecule (Figure 4.3a). As the area per molecule decreases, the films exhibit large crack-like domains. These cracks grow throughout the compression and the film exhibits inconsistent thickening as shown by the sporadic appearance of bright white regions in the film (Figures 4.3b-4.3c). Consistently poor surfactant behavior is observed over the entire range of surface pressures measured for isobutyl-POSS.

In the case of the trisilanol POSS, the films seem uniform (Figures 4.4a-b) until the film approaches collapse, at which point small white domains appear (Figures 4.4c-4.4d). The domains get larger and brighter initially (Figures 4.4e-f) but then slowly revert back to the original small white circles (Figure 4.4g). The eventual return of the smaller domains indicates that a kinetic process is probably taking place and is most likely responsible for the small humps around the collapse point seen in the Π-A isotherms of the trisilanol molecules.
Figure 4.3 – Octasubstituted Isobutyl-POSS BAM Images

a. (Π=0 mN•m⁻¹, A~100 Å²•monomer⁻¹)

b. (Π=0 mN•m⁻¹, A~75 Å²•monomer⁻¹)

c. (Π=10 mN•m⁻¹, A~40Å²•monomer⁻¹)

d. (Π=25 mN•m⁻¹, A~35Å²•monomer⁻¹)

All scales correspond to 500 µm
Figure 4.4 – Heptasubstituted Isobutyltrisilanol-POSS BAM Images

a. ($\Pi=0 \text{ mN} \cdot \text{m}^{-1}$) $A \approx 250 \text{Å}^2 \cdot \text{molecule}^{-1}$

b. ($\Pi=5 \text{ mN} \cdot \text{m}^{-1}$) $A \approx 175 \text{Å}^2 \cdot \text{molecule}^{-1}$

c. ($\Pi=15 \text{ mN} \cdot \text{m}^{-1}$) $A \approx 150 \text{Å}^2 \cdot \text{molecule}^{-1}$

d. ($\Pi=16 \text{ mN} \cdot \text{m}^{-1}$) $A \approx 160 \text{Å}^2 \cdot \text{molecule}^{-1}$

e. ($\Pi=18 \text{ mN} \cdot \text{m}^{-1}$) $A \approx 150 \text{Å}^2 \cdot \text{molecule}^{-1}$

f. ($\Pi=20 \text{ mN} \cdot \text{m}^{-1}$) $A \approx 50 \text{Å}^2 \cdot \text{molecule}^{-1}$

g. ($\Pi=20 \text{ mN} \cdot \text{m}^{-1}$, $A \approx 50 \text{Å}^2 \cdot \text{molecule}^{-1}$)

All scales correspond to 500 µm
The quasistatic compression of octasubstituted isobutyl-POSS shows film instability in the form of dips in the surface pressure as the film was allowed to relax for 300 seconds after being compressed at 20 cm² intervals (Figure 4.5). If the film was allowed to relax for several hours at the conclusion of the compression, the surface pressure returned to 0 mN•m⁻¹. The same is true of the collapsed heptasubstituted isobutyltrisilanol-POSS films. As the film was allowed to relax for 300 seconds after being compressed at 20 cm² intervals, the surface pressure dropped by small amounts in the liquid phase for Π~6 mN•m⁻¹ (Figure 4.6). However, for higher surface pressure and especially in the collapse region of the film, the instability of the surface pressure increased dramatically. This trend was enhanced as the area per molecule was reduced further. When the film was allowed to relax for several hours after the conclusion of the compression in the collapsed regime, the surface pressure returned to 0 mN•m⁻¹. An analog to the octasubstituted isobutyl-POSS, cyclopentyl-POSS, was examined in this manner as well. Its behavior was very similar to that of the isobutyl-POSS (Figure 4.7). Again, instability was observed in the quasistatic isotherm with a surface pressure relaxation back to 0 mN•m⁻¹ over time.

4.2 Blending of Isobutyl-POSS with Poly(vinylacetate) (PVAc)

The water subphase is a good solvent for PVAc so throughout the experiment water is being squeezed out of the swollen polymer chains. ¹³⁰ This process is indicative of strong interactions with the subphase that affect surface behavior. This effect is characterized by the presence of a liquid expanded phase in this system as shown by the Π-A isotherms of PVAc and its combinations with isobutyl-POSS. The Π-A isotherm of a 35 wt% solution of isobutyl-POSS/PVAc was plotted along with isotherms for the two pure components (Figure 4.8). A somewhat unexpected result was obtained in that the isotherm of the two-component solution was shifted to the left of both pure components. To confirm this result, a solution of 75 wt% isobutyl-POSS/PVAc was plotted. The magnitude of the leftward shift was even greater (Figure 4.9). It is important to point out that the area per molecule appears to be too small in both of these cases. This observation is a result of the average area per monomer calculation which is input at the start of the experiment. This number is used to determine the cross-sectional area per
Figure 4.5 – Quasistatic Compression Isotherm of Isobutyl-POSS
Figure 4.6 – Quasistatic Compression Isotherm of Isobutyltrisilanol-POSS
Figure 4.7 – Quasistatic Compression Isotherm of Cyclopentyl-POSS

![Graph showing the quasistatic compression isotherm of Cyclopentyl-POSS. The graph plots \( \Pi / \text{mN.m}^{-1} \) versus \( \langle A \rangle / \text{Å}^2 \cdot \text{molecule}^{-1} \).]
Figure 4.8 – Π-A Isotherm of 35 wt% Isobutyl-POSS with PVAc
Figure 4.9 – Π-A Isotherm of 75 wt% Isobutyl-POSS with PVAc
monomer on the surface at a given surface pressure according to the equation
\[
\langle A \rangle = \frac{A_{\text{trough}} (\text{mm}^2)}{C_{\text{solution, total}} (\text{g} / \text{L}) \cdot V_{\text{spread}} (\text{L})} \cdot \frac{\langle MW_{\text{monomer}} \rangle (\text{g/mol}) \cdot 1 \cdot 10^{14} \cdot A^2}{6.02 \cdot 10^{23} \cdot 1 \text{mm}^2} \tag{4-1}
\]
where \( \langle A \rangle \) is the area per monomer, \( C \) in the total solution concentration, \( V \) is the volume of solution spread, and \( \langle MW \rangle \) is the average monomer molecular weight. The average area per monomer in a binary mixture, \( \langle A \rangle \), is calculated using the mole fractions, \( X_1 \) and \( X_2 \), and the areas per molecule of the pure components at a given surface pressure, \( A_1(\Pi) \) and \( A_2(\Pi) \), according to the equation
\[
\langle A(\Pi) \rangle = X_1 A_1(\Pi) + X_2 A_2(\Pi) \tag{4-2}
\]
In this case, the average area per monomer was calculated assuming that both isobutyl-POSS and PVAc were on the surface during the experiment. The small area per molecule seems to indicate very strong attractive interactions or, more likely, that one of the components is missing from the interface. By recalculating the average area as if only PVAc were present on the surface, the curves shift back to the right along the abscissa and line up with the isotherm of pure PVAc. This information means that the POSS must be collapsing out of the film at the start of the liquid expanded phase leaving only PVAc on the surface. The isotherms also show that as the weight percent of isobutyl-POSS is increased, the normal collapse behavior of the PVAc begins to disappear. The behavior shown by these isotherms is a sign that the POSS and PVAc are not significantly mixing at A/W.

Again, supplementary examination of the 35 wt% system was conducted with BAM. At large areas per molecule, millimeter scale domains of isobutyl-POSS and PVAc are clearly visible (Figure 4.10a). As the film is compressed, the domains remain very large but become more separated (Figure 4.10b). The isobutyl-POSS aggregates into long, vein-like domains within the light colored PVAc matrix (Figure 4.10c). These domains continue to aggregate until the darker isobutyl-POSS completely collapses out of the film at \( \Pi = 18 \text{ mN}\cdot\text{m}^{-1} \) (Figure 4.10d). The large aggregates seen in the BAM images support the hypothesis that the isobutyl-POSS is not readily mixing with the PVAc.
Figure 4.10 – 35 wt% Isobutyl-POSS with PVAc BAM Images

a. (\( \Pi = 0 \text{ mN}\cdot\text{m}^{-1}, A \approx 60\text{Å}^2\cdot\text{monomer}^{-1} \))

b. (\( \Pi = 5 \text{ mN}\cdot\text{m}^{-1}, A \approx 28\text{Å}^2\cdot\text{monomer}^{-1} \))

c. (\( \Pi = 10 \text{ mN}\cdot\text{m}^{-1}, A \approx 20\text{Å}^2\cdot\text{monomer}^{-1} \))

d. (\( \Pi = 18 \text{ mN}\cdot\text{m}^{-1}, A \approx 17\text{Å}^2\cdot\text{monomer}^{-1} \))

All scales correspond to 500 \( \mu \text{m} \)
4.3 Blending of Isobutyl-POSS with Poly(dimethylsiloxane) (PDMS)

The water subphase is a poor solvent for PDMS. Therefore the polymer chains inherently exclude water which leads to the well-defined liquid condensed phase seen in the Π-A isotherms of PDMS and its combination with isobutyl-POSS. The blending behavior of the octafunctional isobutyl-POSS with PDMS was examined and the compression isotherm of a 35 wt% isobutyl-POSS/PDMS solution showed several interesting features. The surface behavior of the two-component solution lies between that of pure PDMS and pure POSS (Figure 4.11). The average cross-sectional area per monomer of the 35 wt% solution at the surface is increased to about 30 Å²/monomer from the 20 Å²/monomer occupied by a pure PDMS monomer. The intermediate position of the isobutyl-POSS/PDMS mixed isotherm between the pure components may also indicate compatibility as surface properties of both pure components appear to be present in the two-component solution. It should also be noted that three transitions not present in the isotherms for either the pure PDMS or the pure isobutyl-POSS are observed in the 35 wt% isobutyl-POSS/PDMS isotherm.

Another interesting observation from Figure 4.11 is the strong discrepancy between the ideal mixing curve (solid circles) and the values observed experimentally. This information suggests that PDMS helps break up the POSS aggregates at A/W. If the POSS is no longer aggregating into a three dimensional structure, all of the POSS may be at the surface. Hence, A_{POSS(Π)} used to calculate <A> in equation 4-1 would be too small. A better value of A_{POSS(Π)} would be the value from the trisilanol-POSS derivative. Using these values, the agreement between the observed mixture and the new calculated "ideal" values is extremely good (see Figure 4.15, solid circles, which would also apply in this case).

The 35 wt% system was examined further using BAM. The images taken at low surface pressures show large branched domains of PDMS and isobutyl-POSS on a dark subphase surface (Figure 4.12a). As the area per molecule is reduced, the branched domains pack closer together (Figure 4.12b) finally resulting in very large white aggregates of PDMS and isobutyl-POSS just before the liquid condensed phase (Figure 4.12c). During the compression of the liquid phase, the isobutyl-POSS and the PDMS components of the film are equivalent in thickness (1-2 nm). The isobutyl-POSS is
Figure 4.11 – Π-A Isotherm of 35 wt% Isobutyl-POSS with PDMS
Figure 4.12 – 35 wt% Isobutyl-POSS with PDMS BAM Images

a. ($\Pi=0$ mN•m$^{-1}$, $A\sim 75\text{Å}^2$•monomer$^{-1}$)

b. ($\Pi=0$ mN•m$^{-1}$, $A\sim 50\text{Å}^2$•monomer$^{-1}$)

c. ($\Pi=0$ mN•m$^{-1}$, $A\sim 40\text{Å}^2$•monomer$^{-1}$)

d. ($\Pi=4$ mN•m$^{-1}$, $A\sim 30\text{Å}^2$•monomer$^{-1}$)

e. ($\Pi=7$ mN•m$^{-1}$, $A\sim \text{Å}^2$•monomer$^{-1}$)

f. ($\Pi=8$ mN•m$^{-1}$, $A\sim \text{Å}^2$•monomer$^{-1}$)

All scales correspond to 500 µm
evenly distributed in smaller domains throughout the darker PDMS matrix (Figure 4.12d). As the film is compressed even further, the POSS seems to be collapsing into large white domains (Figure 4.12e). However, the evenly distributed POSS is still visible at a surface pressure of 7 mN•m⁻¹. As the surface pressure approaches 8 mN•m⁻¹, the PDMS starts to collapse as well. At this point the thickness of the two components approach one another again and an arrangement similar to that seen at Π=4 mN•m⁻¹ is visible (Figure 4.12f). Now all the domains are about 2-3 nm thick. The appearance of the well-dispersed domains of POSS provides evidence for the hypothesis that the isobutyl-POSS forms better blends with PDMS at A/W than PVAc.

4.4 Blending of Isobutyltrisilanol-POSS with Poly(vinylacetate) (PVAc)

As discussed in section 4.1, the behavior of heptasubstituted trisilanol-POSS at the surface is different from that of octasubstituted POSS due to the presence of three hydroxyl groups on one corner of the molecule. This structural difference makes its blending behavior with PVAc potentially interesting. Since the isobutyltrisilanol-POSS molecule and PVAc both have stronger interactions with the water subphase, blending is more likely to occur between those two components than between the PVAc and octasubstituted POSS where no compatibility was observed. A dramatic difference from the isobutyl-POSS/PVAc system is apparent in the Π-A isotherm of a 50 wt% isobutyltrisilanol-POSS/PVAc solution (Figure 4.13). The isotherm of the two-component solution now lies between the two pure component isotherms instead of being shifted to the left as in the PVAc/octasubstituted-POSS system. The average area per monomer does not increase substantially with the addition of the trisilanol-POSS. The shape of the isotherm resembles that of PVAc and lacks the collapse characteristics of the pure PVAc or the pure isobutyl trisilanol-POSS isotherms. As discussed above, the intermediate position of the two-component curve suggests potential compatibility.

BAM images of the 50 wt% isobutyltrisilanol-POSS/PVAc solution show a largely homogeneous film (Figure 4.14a-e) up until the collapse pressure of the POSS. Small white circular POSS domains appear at surface pressures around 20 mN•m⁻¹ (Figure 4.14f). The domains become thicker with additional compression but remain well dispersed throughout the polymer matrix. The large domains present at the end of
Figure 4.13 – $\Pi$-A Isotherm of 50 wt% Isobutyltrisilanol-POSS with PVAc
Figure 4. 14 – 50 wt% Isobutyltrisilanol-POSS with PVAc BAM Images

a. (Π=0 mN•m⁻¹, A~60Å²•monomer⁻¹)
b. (Π=5 mN•m⁻¹, A~45Å²•monomer⁻¹)
c. (Π=7 mN•m⁻¹, A~42Å²•monomer⁻¹)
d. (Π=10 mN•m⁻¹, A~40Å²•monomer⁻¹)
e. (Π=15 mN•m⁻¹, A~35Å²•monomer⁻¹)
f. (Π=20 mN•m⁻¹, A~33Å²•monomer⁻¹)
g. (Π=25 mN•m⁻¹, A~30Å²•monomer⁻¹)
h. (Π=27 mN•m⁻¹, A~28Å²•monomer⁻¹)
i. (Π=29 mN•m⁻¹, A~25Å²•monomer⁻¹)

All scales correspond to 500 µm
the compression are believed to be residual liquid phase which can be eliminated by allowing the film to relax in a quasistatic experiment. The circular domains visible at large areas per molecule (Figure 4.14b-c) form and grow but then disappear as the molecules move into the liquid expanded phase (Figure 4.14d-e).

**4.5 Blending of Isobutyltrisilanol-POSS with PDMS**

The nature of the blending behavior between heptasubstituted isobutyltrisilanol-POSS and PDMS was determined using a 50 wt% solution of trisilanol-POSS/PDMS. The POSS component has a stronger affinity for the water subphase than the PDMS chains in this case. This difference may be expected to lead to a film in which the PDMS collapses while the isobutyltrisilanol-POSS remains on the surface leading to an isotherm that shifts to a smaller area as seen in the non-blending isobutyl-POSS/PVAc system. In contrast, the Π-A isotherm of the 50 wt% blend lies between the pure components and is nearly identical to what one would expect from ideal mixing (Figure 4.15). Transitions visible in both the pure PDMS and pure isobutyltrisilanol-POSS are visible in the two-component isotherm. The collapse of the PDMS component occurs before the collapse of the POSS due to the difference in their interactions with water.

BAM images of the 50 wt% isobutyltrisilanol-POSS/PDMS system show a homogeneous film at large areas per monomer (Figure 4.16a). Domains do not appear at the collapse pressure of PDMS (Figure 4.16b) but do start to appear as light circles near the collapse pressure of the trisilanol-POSS (Figure 4.16c). These white domains become denser and larger as the film collapses (Figure 4.16d-f). As in the trisilanol-POSS/PVAc system, some residual liquid domains, characterized by larger dark areas, are present in the collapsed film. It is likely that these would be eliminated if the film's surface pressure was allowed to relax.

**4.6 PDMS/POSS Copolymer Architecture Effects**

After characterizing the surface behavior of blends of PDMS and octasubstituted isobutyl-POSS, a preliminary investigation of copolymers of PDMS and POSS derivatives was initiated at A/W. A graft copolymer of PDMS with cyclohexyl-POSS grafts (Figure 4.17a) was studied as a function of the weight percent of the grafts. A bead copolymer with both cyclopentyl-POSS and PDMS in the backbone (Figure 4.17b) was also examined. The Π-A isotherms of these copolymers show a behavior that is greatly
Figure 4.15 – Π-A Isotherm of 50 wt% Isobutyltrisilanol-POSS with PDMS
Figure 4.16 – 50 wt% Isobutyltrisilanol-POSS with PDMS BAM Images

Image c was taken just before the collapse of the trisilanol-POSS. Images d, e, and f were taken during and after the small "hump" visible in the Π-A isotherm. All scales correspond to 500 µm.
Figure 4.17 – General Structure of PDMS/POSS Graft Copolymer

a. Graft Copolymer

b. Bead Copolymer
Figure 4.18 – Π-A Isotherms of PDMS/POSS Graft Copolymers

![Graph showing Π-A Isotherms of PDMS/POSS Graft Copolymers]

- 5 wt% Cyclohexyl Graft
- 40 wt% Cyclohexyl Graft
- Pure PDMS
affected by the amount of POSS (Figure 4.18). At 5 wt% POSS, the graft's surface activity is very similar to pure PDMS. However, by increasing the POSS graft content to 40 wt%, the behavior changed drastically. All of the normal collapse behavior of PDMS, seen at about $\Pi = 8 \text{ mN} \cdot \text{m}^{-1}$, is absent. There is also a change in slope occurring at a surface pressure of $5 \text{ mN} \cdot \text{m}^{-1}$ suggesting the possible existence of more than one liquid phase.

When comparing the 40 wt% graft to the thirty-five weight percent blend, the $\Pi - A$ isotherms are also quite different (Figure 4.10). Even at similar weight percentages of POSS, the surface tension of the blended system is still behaving the same way as pure PDMS. It is important to recall that the size and hydrophobicity of the R group on the octasubstituted POSS has no predictable effect on its behavior at A/W so the comparison between the isobutyl-POSS in the blended system and the cyclohexyl-POSS in the graft copolymer is legitimate.

In the case of the bead copolymer, with one POSS unit for every 4.9 PDMS repeat units, the POSS content is 73% by weight. None of the characteristic PDMS behavior is seen in the bead copolymer isotherm (Figure 4.19). It is also very different from both the graft and the blend systems. There is no visible collapse behavior due to the PDMS.

Quasistatic isotherm experiments similar to those discussed in section 4.1 were conducted using graft copolymers with different functional groups. A 40 wt% cyclohexyl-POSS/PDMS graft copolymer film, that was compressed at 20 cm$^2$ intervals and allowed to relax for 300 seconds, showed slight instability throughout the liquid region even through the change in slope seen at $\Pi = 5 \text{ mN} \cdot \text{m}^{-1}$ (Figure 4.20). Again, complete relaxation to zero surface pressure after film collapse was observed over a few hours time. A 40 wt% graft copolymer of cyclopentyl-POSS with PDMS showed greater film stability below the initial change in slope at 5 mN$\cdot$m$^{-1}$ but the surface pressure became much more unstable at higher surface pressures (Figure 4.21). After several hours, the surface pressure relaxed to 0 mN$\cdot$m$^{-1}$ after film collapse in a fashion similar to the other examples.
Figure 4.19 – Π-A Isotherm of a PDMS/POSS Bead Copolymer
Figure 4.20 – Quasistatic Compression Isotherm of a 40 wt % Cyclohexyl-POSS/PDMS Graft Copolymer
Figure 4.21 – Quasistatic Compression Isotherm of a 40 wt % Cyclopentyl-POSS/PDMS Graft Copolymer
CHAPTER 5
Poly(1-alkene-alt-maleic anhydride) Derivatives (PXcMA)

5.1 Langmuir-Blodgett Films of Maleic Anhydride Derivatives

Alkenes can react with maleic anhydride to produce a wide variety of copolymers with different functional groups. Langmuir-Blodgett (LB) films of maleic anhydride derivatives have shown potential as electron beam resists when copolymerized with polystyrene. Thin films of these materials can also be made by spincoating or by casting from solution or the molten state. The incorporation of azobenzene sidegroups introduces birefringence when the cast films are exposed to polarized light. By varying the side chains at the R₁ position (Figure 5.1), the effect of alkyl chain length on the viscoelasticity of monolayers at the air/water interface has also been examined.

Langmuir-Blodgett films of poly(1-alkene-alt-maleic anhydride) (PXcMA) derivatives were deposited onto silicon wafer substrates. The wafers were cleaned according to the procedure discussed in Chapter 2. Π-A isotherms were measured prior to deposition for all the derivatives (Figure 5.2) and determined to be in good agreement with those measured previously. The isotherms were then used to determine the appropriate film pressure for deposition of each of the films.

Layers of poly(1-hexen-alt-maleic anhydride) (PHcMA) were transferred at a surface pressure of 15 mN•m⁻¹. The transfer was shown to be z-type as the monolayer only deposited in the upward direction with an average upward transfer ratio of 0.832. Recalling that perfect deposition of exactly one monolayer is characterized by a transfer ratio equal to one, the ratio of 0.83 shows that almost one monolayer is deposited each time the wafer passes through the monolayer in the upward direction. However, the average transfer ratio in the downward direction was equal to –0.43. This means that for every monolayer deposited in the upward direction, almost half of it was being pulled off as the film passed through the monolayer in the downward direction. This means that even though 40 layers were theoretically transferred, only about 20 actually remained on the substrate after the deposition was completed. This gives an approximate film thickness of 150 Å calculated from the size of the PHcMA molecule (~8-10 Å•monolayer⁻¹). The film was very light and non-homogeneous.
Figure 5.1 – General Poly(1-alkene-alt-maleic anhydride) (PXCMA) Structure

Structure at pH = 2, $R_1$ equals $C_4H_9$ (PHcMA), $C_6H_{13}$ (POcMA), $C_8H_{17}$ (PDcMA), and $C_{16}H_{33}$ (PODcMA)
Figure 5.2 - Π-A Isotherms of PXcMA Derivatives

![Graph showing Π-A Isotherms of PXcMA Derivatives](image)

- PHcMA
- POcMA
- PODcMA
- PDcMA
A similar transfer pattern was observed for poly(1-octene-alt-maleic anhydride) (POcMA) where layers were deposited in the upward direction but then were partly removed in the downward direction when transferred at a surface pressure equal to 20 mN•m\(^{-1}\). In this case, the average transfer ratio for the upward passes was equal to 1.13 indicating good monolayer transfer in that direction. The average transfer ratio for the downward passes was –0.28. Again, some of the layer deposited in the upward direction was removed during the wafer's downward pass through the monolayer. Twenty layers were theoretically transferred but only about 17 remained at the end of the deposition. This gives a film thickness roughly equal to 200Å calculated from the size of the molecule (~10-15 Å•monolayer\(^{-1}\)). The POcMA film was also non-homogeneous and barely visible.

The film resulting from the transfer of the poly(1-decene-alt-maleic anhydride) (PDcMA) was dark and uniform in appearance. The PDcMA layers were transferred at a surface pressure of 25 mN•m\(^{-1}\). The average transfer ratio in the upward direction was equal to 0.88 while the average transfer ratio in the downward direction was equal to 0.34. The existence of a positive transfer ratio in the downward direction indicates that the film deposited in the upward direction is not being removed as was the case for the two previous derivatives. A nearly perfect monolayer is being transferred onto the substrate in the upward direction in this case while some residual molecules are being transferred in the downward direction. This results in a film that is nearly half the intended thickness, due to significant transfer on only every other pass through the monolayer. The resulting film is theoretically only about 300 Å thick calculated from the size of the molecule (~15-20 Å•monolayer\(^{-1}\)). The film is dark and uniform in appearance. This result is surprising because it has been reported in the literature that alkyl side chains must be at least fourteen carbons long in order to form transferable films and the alkyl chain of this derivative is only eight carbons long.\(^{11}\)

A uniform film also resulted from the deposition of poly(1-octadecene-alt-maleic anhydride) (PODcMA) transferred at a surface pressure of 15 mN•m\(^{-1}\). The average transfer ratio in the upward direction was equal to 0.84 while the average transfer ratio in the downward direction was equal to 0.73. This designates that significant transfer occurred on each pass of the wafer through the monolayer surface resulting in \(y\)-type
deposition. The wafer was dipped for 40 cycles, with one cycle being both the upward and downward pass, resulting in approximately 80 layers of material. The resulting film is blue, very dark, and uniform. The blue color results from the thickness of the film, approximately 2000 Å calculated from the size of the molecule (~25-30 Å•monlayer⁻¹).

5.2 Alternating Film Deposition

After determining that the PHcMA, POcMA, and PDcMA derivatives exhibited ζ-type deposition, the transfer of a monolayer was attempted using an alternating method. This method is advantageous because the layers can be deposited in only one direction. Using the alternating method, the wafers were passed through a surface of pure water on each downward pass and through the PXcMA monolayer on the upward pass. It is important to note that the transfer ratio is not measured for the downward pass through the pure 0.01M HCl solution so it is difficult to tell if the monolayer is being removed in the same manner as it was when the wafer passed through the monolayer in the downward direction. In order to help prevent this, the wafer was allowed to dry for two minutes between each upward and downward pass.

The alternating deposition of PHcMA produced transfer ratios in the upward direction comparable to those measured conventionally. However, it was noted during the experiment that the pure 0.01M HCl subphase was wetting the wafer on the downward pass. This wetting makes it possible for the subphase to get under the newly deposited layer and remove it. After several layers were deposited, a portion of the wafer was exposed to solvent. There was no qualitative difference between the areas of the wafer where the film would have been dissolved and the areas that should have remained film-covered. This observation indicates that the layers were removed by the subphase just as they were by the monolayer during the conventional deposition. Similar results were observed for POcMA.

The alternating deposition of PDcMA produced transfer ratios in the upward direction comparable to those measured conventionally showing that the transfer was quantitative. Additionally, the partial transfer of the polymer in the downward direction was eliminated using this technique resulting in an organized film. During the downward pass, there was no observed wetting of the wafer by the 0.01M HCl subphase. Uniform films were obtained.
The transfer behavior observed for these polymers can be further explained using scaling exponents. By plotting the log of the surface pressure vs. the log of the area per monomer, a linear plot is generated in the region $\Pi = 1\text{-}5 \text{ mN} \cdot \text{m}^{-1}$. The negative slope of each line provides the scaling through the equation

$$\Pi = CA^{-z}$$

where $\Pi$ equals the surface pressure, $C$ is a proportionality constant, $A$ is the area per monomer, and $z$ is the scaling exponent. The scaling exponent $z$, can be related to the critical exponent for the correlation length, $\nu$, through the relationship

$$z = \frac{2\nu}{2\nu - 1}.$$  

For polymers, $\nu$ is related to the radius of gyration ($R_g$) of the polymer and is a function of the degree of solvation. For different degrees of solvation, $R_g \sim N^\nu$, where $N$ is the number of repeat units in the polymer. For theta solvent conditions, $\nu$ in two dimensions is approximately equal to 0.5 for a mean field treatment so the slope of the line goes to infinity. For good solvent conditions, $\nu$ in two dimensions is approximately equal to 0.77 for a mean field treatment and the slope of the line approaches 3. The values of $z$ for the of the PXcMA derivatives are $\sim 7.5$ for PHcMA, $\sim 14.3$ for POcMA, $\sim 35.3$ for PDcMA, and $\sim 37.0$ for PODcMA. This data indicates that the water subphase is a poor solvent for all the derivatives but is a much better solvent for PHcMA and POcMA than for PDcMA or PODcMA. This difference is readily apparent in both the $\Pi$-$A$ isotherm and the LB transfer behavior in the form of a more expanded liquid region as well as the inability to form PHcMA multilayers by $z$- or $y$-type deposition. As the length of the hydrocarbon chain goes up, the scaling exponent increases which translates into increasingly poor solvent conditions at $A/W$ and a lesser degree of chain swelling. The increase in the scaling exponent also translates to greater elasticity as the surface dilational elasticity is nothing more than

$$\varepsilon_d = \kappa_s^{-1} = -A \left( \frac{\partial \Pi}{\partial A} \right)_r$$

where $\kappa_s$ is the surface analog to the bulk isothermal compressibility. As noted in Chapter 1, viscoelasticity and hydrophobicity are two major factors in LB-film formation.
CHAPTER 6

Conclusions

Using interfacial tension measurements, the critical micelle concentration (c.m.c.) of the poly(dimethylsiloxane-b-(3-cyanopropyl)methylsiloxane-b-dimethylsiloxane) (PDMS-PCPMS-PDMS) series of triblock copolymers was determined to be about 0.001 g•L⁻¹. The c.m.c. was also determined to be about 0.001 g•L⁻¹ by dynamic light scattering (DLS). Temperature was shown to have no significant effect on the c.m.c. in the range of 25°C through 45°C for this polymer. The c.m.c. was determined to be between about 0.0001 and 0.001 g•L⁻¹ by interfacial tension for a poly(dimethylsiloxane-b-2-ethyl-2-oxazoline) (PDMS-PEtOx) diblock copolymer. These measurements ensured that the synthesis of cobalt nanoparticle dispersions for potential biomedical applications was occurring above the c.m.c.

Octasubstituted and heptasubstituted polyhedral oligomeric silsesquioxane (POSS) derivatives were shown to have very different behavior at the air/water interface. The two derivatives have different subphase affinities that alter their organization at A/W. The octasubstituted POSS is a poor surfactant and the application of small lateral pressures causes it to collapse at the surface. Poor subphase affinity causes octasubstituted POSS to aggregate into films that have an area per molecule at A/W roughly three times smaller than the trisilanol derivatives even though both molecules have nearly identical theoretical sizes. Consequently, the octasubstituted POSS derivatives must have a thickness that is three times larger than the trisilanol derivatives. The heptasubstituted trisilanol-POSS is a better surfactant than the octasubstituted derivative due to its enhanced subphase affinity. The hydroxyl groups present on one corner of the silsesquioxane cage increase the affinity of the trisilanol derivative for the water subphase allowing it to stay on the surface until large lateral pressures (~20 mN•m⁻¹) are applied before collapsing into multilayers. Therefore, the size of the trisilanol molecule (~200 Å²) is closer to the true size of the POSS molecules on the surface. As bulkier, more hydrophobic, functional groups are added to the trisilanol molecule, the attraction between the hydroxyl groups and the water subphase is overcome and lower collapse pressures are observed. This effect is absent for the octasubstituted derivatives as nothing is holding it to the surface during the compression regardless of
side groups. Both the octasubstituted and the heptasubstituted POSS derivatives exhibit instability as the surface pressure of both will fall back to 0 mN•m⁻¹ upon compression into the collapsed regime over long enough times.

No significant mixing was observed for the isobutyl-POSS/PVAc system at A/W. The presence of large, millimeter size, POSS aggregates in the PVAc matrix, as seen with BAM, persisted throughout the lateral compression. The Π-A isotherms show a shift of the mixed curves to smaller areas per molecule than the pure curves. It can be concluded, then, that the POSS collapses almost immediately upon compression of the film. However, mixing was observed for the isobutyl-POSS/PDMS system. The Π-A isotherm is between those of the pure components and small well-dispersed domains were observed in the liquid regime with BAM.

Isobutyltrisilanol-POSS exhibits surface compatibility with PVAc at A/W. A homogeneous film is present until the collapse of the POSS at which point small, well-dispersed, domains are visible. This observation is expected because of the increased surface affinity of the trisilanol-POSS due to the hydroxyl groups present on the siloxane cage. The presence of the hydroxyl groups also increases structural similarity between PVAc and trisilanol-POSS favoring the enhanced mixing observed. Isobutyltrisilanol-POSS and PDMS are initially compatible through the collapse of the PDMS at Π~8 mN•m⁻¹ resulting in a homogeneous film as seen with BAM. The collapse of the trisilanol-POSS occurs at Π~18 mN•m⁻¹ and results in the formation of small, well-dispersed, domains. In this system, the surface affinity of the trisilanol-POSS is greater than that of the PDMS due, again, to the presence of the hydroxyl groups on the POSS cage.

POSS/PDMS copolymer architecture greatly affects surface behavior at A/W. The Π-A isotherm of a 5 wt% cyclohexyl-POSS/PDMS graft copolymer shows surfactant characteristics similar to pure PDMS. However, increasing the wt% of POSS in the copolymer changes the isotherm's shape. Despite similar weight percents of POSS, the 40 wt% cyclohexyl-POSS/PDMS graft copolymer performs very differently from the mixed 35 wt% isobutyl-POSS/PDMS system. While the mixed system behaves like PDMS, the graft copolymer does not exhibit any PDMS-type characteristics. Its liquid region is very expanded and the collapse is not observed even at surface pressures twice that of the
collapse of PDMS. The bead copolymer with both cyclopentyl-POSS and PDMS in the backbone is also different from pure PDMS. A clear collapse is not observed even at pressures well above the collapse of PDMS. However, the films at high surface pressures for both the high wt% graft and bead copolymers are unstable. If compression ceases at the highest $\Pi$ values, the films will relax back to $\Pi=0 \text{ mN} \cdot \text{m}^{-1}$ after several hours.

PHcMA exhibits pseudo z-type deposition onto a hydrophobic substrate. Films stick to the wafer on the upward stroke but poor film adhesion results in layers being removed during the downward pass of the wafer through the monolayer. The resulting films are non-uniform and practically invisible although the presence of some film is observed at random spots on the substrate. The same is true of the POcMA derivative. The films are similar in appearance to those of the PHcMA derivative. However, PDcMA appears to exhibit true z-type deposition onto hydrophobic substrates despite the alkyl side-chain being only eight carbons long. Alternating deposition of the PDcMA derivative results in homogeneous multilayer films. PODcMA has an alkyl chain that is sixteen carbons long and results in y-type deposition as expected. The resulting films are very uniform and can have controlled thickness.

Alternating deposition of the PHcMA derivative produced similar films to those deposited by the single trough instrument. The wetting of the wafer by the subphase indicated that the layers were being removed on the downward pass just as they were by the monolayer in the single trough deposition. Analogous results are suspected for the POcMA derivative. The PDcMA derivative was deposited only on the upward pass and resulted in uniform films with transfer ratios similar to those measured using the single trough deposition method.
CHAPTER 7
Suggestions for Future Work

The characterization of poly(dimethylsiloxane-b-2-ethyl-2-oxazoline) (PDMS-PEtOx) can continue to include molecular weight studies similar to those conducted with poly(dimethylsiloxane-b-(3-cyanopropyl)methylsiloxane-b-dimethylsiloxane) (PDMS-PCPMS-PDMS). Experiments can also be conducted to determine the temperature dependence of the c.m.c. for this diblock copolymer. Dynamic light scattering could be used to determine the hydrodynamic radius of the diblock copolymer micelles. The oxazoline block adheres well to both the cobalt metal and to silica surfaces through hydrogen bonding. The good adhesion with silica has potential importance in increasing the oxidative stability of the cobalt nanoparticles in a PDMS carrier fluid. Preventing the oxidation of the cobalt is important to this system's biocompatibility. By adding a silica layer to the nanoparticles, oxidation can be potentially prevented. Also, by further understanding the micellar behavior of this polymer, silica particles may be included inside the micelle with the cobalt. This modification would prevent oxidation in the body from the inside of the micelle rather than the outside thereby eliminating potential problems of adhering PDMS to silica.

The POSS/PDMS graft and bead copolymers can be observed at A/W with BAM to determine specific phase behavior. This study will aid in differentiating between low and high POSS content graft copolymers and further understanding the differences in their isotherms. The characterization of the graft copolymers can be expanded to include more wt%'s of POSS so that the complete trend can be established. A similar study as a function of POSS content would also be useful in distinguishing the bead copolymer. The graft copolymer has potential applications as a nanocomposite material. The mechanical relaxation characteristics can be studied as a function of wt% of POSS incorporated. It would also be interesting to study the thermal properties of the graft as compared to the homopolymer to determine the graft's usefulness as a thermally protective coating material. These modified linear polymers may also have applications similar to sol-gel systems but without the introduction of chemical crosslinking and processing problems.
The mixing behavior of POSS and PDMS can be further examined by broadening the range of POSS wt% in each sample. The shifting of the Π-A isotherm to larger areas per monomer can then be illustrated and a larger trend established. BAM can then be used to visualize the domains and note any size or distribution changes. By illustrating the wt% POSS dependence on this system, insights into nanofiller behavior in high performance polymers can be made. Dilational studies can also be conducted on the POSS/PDMS system using surface light scattering to observe changes in film elasticity with the addition of filler molecules which would lead to a better understanding of the effect of nanofillers on the mechanical properties of thin polymer films for pressure sensitive and hot-melt adhesives.
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