

RICE UNIVERSITY

Thermodynamics of Confined Colloid-Polymer Mixtures

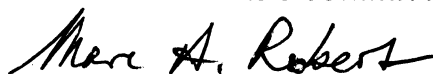
by

Jonathan N. Lo

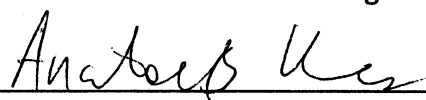
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Abstract

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Recent advances have elucidated the behavior of colloids and polymer systems in the archetypal three dimensions. However, these systems are ill-understood when confined to two dimensions. Using experimental techniques such as Langmuir-Blodgett and ellipsometry, we attempt to explain the behavior of two dimensional colloid/polymer systems via micron-scale imaging as well as measuring their surface-pressure versus area isotherms. Possible phase transition behaviors and mechanisms are uncovered and discussed. We explore the importance of proper colloidal stabilizing ligands in terms of hydrophobic forces and their impact on ellipsometry as well as Langmuir-Blodgett experiments. Lastly, we give insight for future work that still remains to be done in this area.

Chapter 1: Introduction

In their own rights, both colloids and polymer systems have been ubiquitous in technology for many decades. For example, in biosciences, dispersed gold nanoparticles have been studied as novel agents for use in the fight against cancer (El-Sayed, Huang and El-Sayed 2002), as well as vessels for use in drug and gene delivery (Soppimath, et al. 2001). Colloid self-assembly has been studied extensively in the context of modern optics and material sciences due to applications in the production of photonic band-gap materials (Glotzer, Solomon and Kotov 2004, Hynnien, et al. 2007). Systems of pure polymer are extremely diverse, having been studied in nearly every modern context within chemical engineering from microfluidic devices (Jensen 2001) to photovoltaics (Li, et al. 2005).

Systems of pure polymer in two dimensions also see wide use within industry as well as academia. Polymer nanosheets and nanowires are being researched as they have broad applications in chemical engineering, from catalysis (Matsui, et al. 2007) to biosensors (Ramanathan, et al. 2005). Commercially, perhaps the most obvious is the role of polymers in the manufacturing of the universal liquid-crystal displays that are used today. In every liquid crystal display, layers of p-ethoxybenzylidene-p'-aminobenzonitrile are aligned in order to confer onto each

screen necessary optical properties to transmit light (Castellano 2006). These, however, are only examples of quasi two-dimensional systems of pure polymer, as the layers of polymer are often hundreds of microns thick. In order to produce polymers confined strictly to two dimensions, the polymer must be dispersed on an interface—such as between air and water—where molecular interactions may force it to lie completely flat. In this manner, angstrom-thick monolayers of polymer can be laid down.

Similarly to polymers, colloids held via surface tension at an interface can also form monolayers (Pieranski 1980). Depending on the concentration, these monolayers have been found in systems of sulfate-polystyrene particles at an oil/water interface to exhibit solid or liquid phases, including the hexatic phases (Lin and Chen 2007). Obviously not all polymers or colloids lie flat on an air/water interface. However, due to many experimental (Pieranski 1980, Oettel 2007, Nikolaidis, et al. 2002) theoretical, and computer simulation (Sun and Stirner 2004, Fenwick, Bresme and Quirke 2001) studies of colloids and polymers, as well as monolayer stability, it is now possible to create well-characterized monolayers of either polymers or colloids.

When a polymer does not naturally form a monolayer at an air/water interface, it is sometimes possible, nevertheless, to obtain one via chemical intervention. Mention can be made of the monolayers of poly(imide) and poly(arylenevinylene), which are prepared using the Langmuir-Blodgett method by attaching hydrophobic side-chains to their polymeric precursors, resulting in a polymer with a hydrophilic backbone and hydrophobic side-chains (Era, et al. 1989, Kakimoto, et al. 1986). Note that the hydrophobicity of the side-chains can often be fine-tuned in order to adjust the conformation of the polymer at the interface. At lower concentrations, both the polymer and its side-chains lie flat upon the

air/water interface, whereas at higher concentrations the side-chains align and point upwards.

This thesis is organized as follows—in Chapter 2, a brief background on the experimental work will be given. In Chapter 3, the researches we have performed, along with our results, are discussed. Lastly, Chapter 4 details the research problems which still need to be tackled.

Chapter 2: Background

In order to better understand the experiments, it is useful to at first briefly discuss the principles of Brewster angle microscopy. Brewster angle microscopy, used in conjunction with the Langmuir-Blodgett trough (Figure 1), will reveal the broad details of coexisting phases, allowing us to discern the long-ranged patterns that are present within the system, as well as areas of disorder (Hoenig and Moebius 1991). Brewster angle microscopy works by shining an incidence beam of plane-polarized (or p -polarized) light onto an air/water interface and recording the angle, known as the *Brewster angle*, at which total internal reflection occurs. When a thin film is added on top of the subphase, the angle of refraction changes, causing the film to reflect the incident light. This reflected light will then be used to generate an image of the air/water interface (Figure 2).

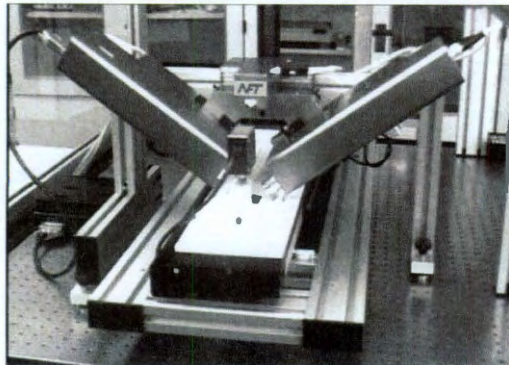


Figure 1: Combined Langmuir-Blodgett trough and Brewster Angle Microscopy setup

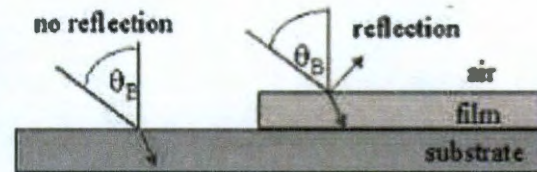


Figure 2: Principle of Brewster Angle Microscopy

To date, there have been two authors whom have made significant contributions to systems of polymer or colloid monolayers. One of whom is A. Amini, whose experiments were performed in our group (Amini and Robert, 2010), as well as Esker and his group of Virginia Tech (Li and Esker 2007). Amini studied a system of poly(L-lactic) acid (PLA) and cadmium selenide nanoparticles (Amini 2010). He chose 790 nm paramagnetic Fe_2O_3 colloids ($q \approx 0.2$) due their hydrophobicity, steric stability, as well as neutral charge. PLA was selected as the polymer because of its hydrophobic backbone and hydrophilic side chains – allowing it to lie completely flat on an air/water interface. A remarkable property of PLA is that when it is sufficiently compressed, it forms 10_3 helicies on the interface. These helicies resist compression and allow PLA to lie flat at the interface rather than buckling or having individual monomer units flip up, resulting in the formation of multilayers (Bourque, et al. 2001, Pelletier and P  zolet 2004).

At first, these experiments, based on the Langmuir-Blodgett method, yielded the surface pressure (π) versus area (A) isotherms. The colloids did not exhibit any transition until the onset of multilayer formation. On the other hand, the isotherms of pure PLA *did* exhibit a liquid-expanded to liquid-condensed transition, in

accordance with previously published results (Ni, Lee, et al. 2006). The experiments determined that the vanishing slope of the PLA transition isotherm supported the theory of a first-order phase transition (Figure 3). Because theory predicts that an isotropic to nematic transition is generally continuous (i.e. second order) in two dimensions, the PLA transition must indeed be an isotropic to smectic transition (de Gennes 1974). The nematic phase, in the situation, is glossed over completely; this phenomena is similar to the process of sublimation in the bulk – or when a substance undergoes phase transition from the solid state directly to the gaseous state.

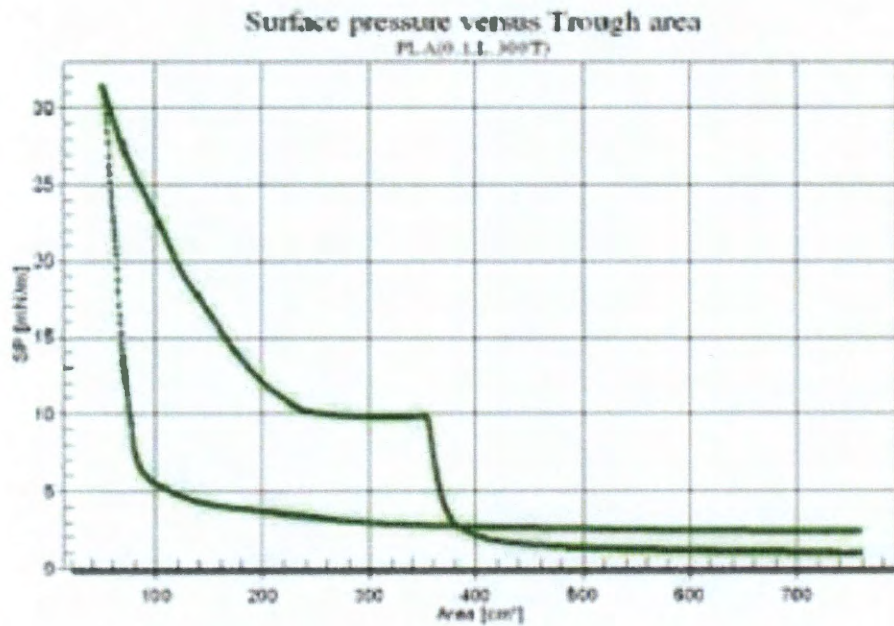


Figure 3: Surface-pressure versus area isotherms for pure PLA at 14.2° C with a full expansion and compression cycle (Amini 2010)

Esker (Ni, Lee, et al. 2006) also did significant imaging of PLA monolayers via ellipsometry. In Esker's experiments, a setup similar to ours was used, wherein 12.9 kg/mol PLLA was spread dropwise onto a Langmuir-Blodgett trough. This entire setup was placed under an ellipsometer and imaged under various degrees of compression, the results of which are shown in the following figure. Subfigure (a) in Figure 2 shows the liquid expanded phase, (b) shows the liquid expanded/liquid condensed coexistence phase, (c) shows the formation of an LC monolayer and finally, (d) shows the onset of film collapse and the formation of multilayers.

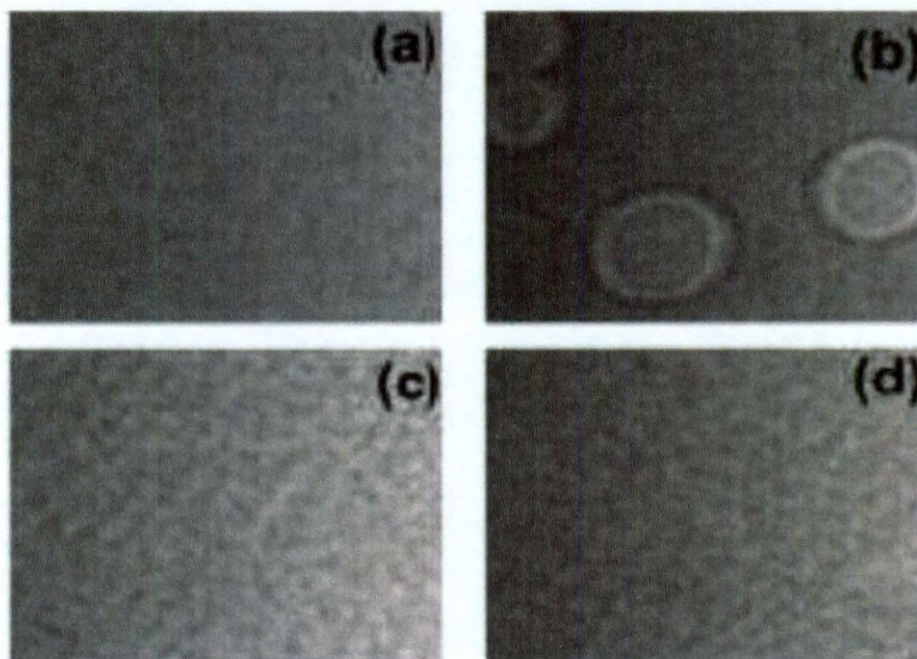


Figure 4: Esker's PLA images (Ni, Lee, et al. 2006).

It is important to briefly touch on depletion interactions, as they play a subtle, but important part in our research. As mentioned in the introduction, the range and strength of colloidal interactions in three dimensions can be greatly affected by the addition of non-adsorbing polymers (Bolhuis, Louis and Hansen 2002). These polymers, when dissolved in a colloidal suspension, cannot approach a colloidal particle too closely, and are excluded from a so called depletion zone, which is a spherical shell of thickness $2R_g$, where r_g is the polymer radius of gyration. When two or more colloidal particles are close to each other, the depletion zones of each individual colloid will overlap, resulting in an unbalanced osmotic pressure and leading to a depletion force which is generally attractive in nature (Figure 5). When the colloidal radius is approximately three times larger than the radius of gyration of the polymer, simple approximate theoretical arguments predict that a phase separation occurs, and the polymers and colloids self-segregate into a polymer-rich phase and a colloid-rich phase (Oosawa and Asakura 1954).

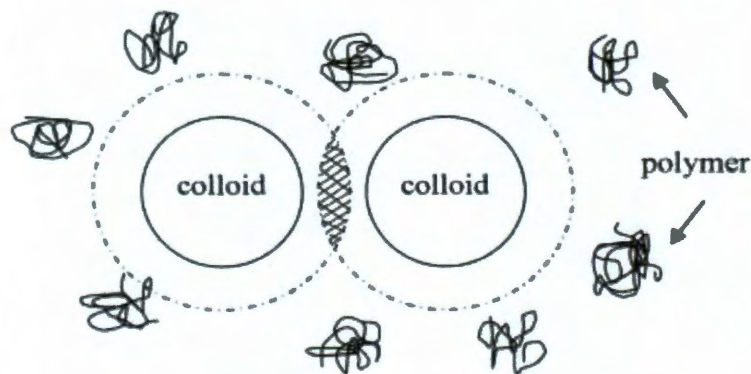


Figure 5: Polymer molecules being excluded from depletion zones (hatched region), leading to an attractive depletion force between colloids

The first model which provides a simple description of depletion interactions is that of Asakura and Oosawa (1954). In the Asakura-Oosawa (AO) model, the colloids are represented as hard spheres of diameter σ , while the polymers have a radius of

gyration r_g and are mutually interpenetrable, but impenetrable to the colloids. This gives rise to the following two-body potentials:

$$U_{HS}(r) = \begin{cases} \infty, & 0 < r < \sigma \\ 0, & r > \sigma \end{cases}$$

$$U_{CP}(r) = \begin{cases} \infty, & 0 < r < \frac{1}{2}(\sigma + 2r_g) \\ 0, & r > \frac{1}{2}(\sigma + 2r_g) \end{cases},$$

where U_{HS} is the colloid-colloid interaction potential and U_{CP} is the colloid-polymer interaction potential. Although this simple model is qualitatively reasonable, the theoretical predictions based on it do not agree well with experimental results on three-dimensional systems. The AO model has been analyzed using various approximations. For example, Gast, Hall, and Russel have used perturbation theory in the canonical ensemble (1983), while Lekkerkerker, Poon, Pusey, Stroobants and Warren (1992) have used a semi-grand canonical ensemble.

Chapter 3: Completed Research and Discussion

3.1 Materials and Methods

Solid poly(l-lactic acid (PLA) of 700,000 g/mol, with polydispersity 1.8 was purchased from Polysciences Inc. and used without any further purification or chemical modification. The three-dimensional radius of gyration (R_g) of PLA was determined via static light scattering.

Peak 1		rms radius moments (nm)	
Peak limits (min)	11.175 - 12.635	Rn	25.7 (4%)
dn/dc (mL/g)	0.055	Rw	29.8 (3%)
A ₂ (mol mL/g ²)	0.000	Rz	35.7 (3%)
UV ext. (mL/(g cm))	0.000		
Model	Zimm		
Fit degree	1		
Injected mass (g)	1.0000e-4		
Calc. mass (g)	2.3972e-5		
Mass Recovery	23.9724 %		
Mass Fraction	100.0000 %		

The two-dimensional R_g was then calculated via Flory-Huggins exponents as follows:

$$R_g \sim N^{\nu_f}, \text{ with } \nu_f = 0.588 \text{ (3D) or } \nu_f = 0.75 \text{ (2D)}.$$

From light scattering, we know $R_g(3D) = 25.7 \text{ nm}$, which implies $N = 249.9$.

Therefore we can conclude that:

$$R_g(2D) = 249.9^{0.75} \approx 62.8 \text{ nm.}$$

For colloids, 6.85 nm (± 0.75 nm) CdSe nanoparticles in chloroform from NN-Labs were used. These particular colloids were chosen due to their insolubility in chloroform, as well as the mutual miscibility of the solvents, and therefore were used without any further modification.

PLA stock solution was prepared by dissolving a few PLA pellets in chloroform within a scintillation vial. The vial was then placed on a hotplate set to 55 degrees Celsius, and the polymer was allowed to dissolve for 24 hours. A stirbar was placed within the scintillation vial to ensure homogeneity, and was set to stir at around 100 RPM. Although the concentration of the stock solution varied from experiment to experiment, it was never more than 2 mg/mL. After 24 hours, the entire stock solution was then filtered using Whatman 50-micron, GD/X PTFE syringe filters to trap and eliminate any undissolved polymer. The mixture was then allowed to sit for 30 minutes, or until it was no longer warm to the touch before it was used for experimentation.

In experiments involving colloids, we used 6.5 nm CdSe nanoparticles produced from NN-Labs. These nanoparticles are suspended in chloroform and have an octadecylamine ligand covalently bonded to the surface for steric stabilization and to prevent aggregation or flocculation. A light scattering experiment was done immediately after receiving the sample to ensure the size of the nanoparticles were indeed 6.5 nm, as advertised. Before each experiment, the entire sample was sonicated for at least one hour to further reduce the chance of flocculation before an appropriately sized sample was spread on the air/water interface.

The Langmuir-Blodgett trough (KSV 3000 from KSV Instruments Ltd.), as well as the barriers were then cleaned thoroughly with 95% ethanol and ultrapure, deionized water (resistivity = 18.2 m Ω). The trough was then filled with the same

water (DI, resistivity = 18.2 mΩ) and a 1.2 cm² Pt Wilhelmy plate with a resolution of 0.004 mN per m² was hung to record the surface tension and positioned such that its latitudinal axis was perpendicular to the barriers. To remove any other contaminants that could have remained, a pipette connected to a pump gently swept the air/water interface before the experiment was performed, removing any residual dust or dirt. The surface was determined to be clean when the background fluctuation of the surface pressure did not exceed 0.01 mN/m.

Our sample of interest is then added to the surface of the Langmuir-Blodgett trough. The optimal amount of sample was then added to the trough using a 50 μL (±1 μL) glass Hamilton gas chromatography syringe, such that there was optimal spreading on the interface. This amount was determined by trial and error and often depends on the materials in question – adding too much would yield a solid multi-layer on the surface and not adding enough would result in measurements of white noise as the surface pressure of the sample was below the resolution of the instrument. In most cases, it was around 100 μL. After a period of fifteen minutes to ensure that all of the solvent had evaporated from the surface, measurements commenced. The effective area of the trough was gradually decreased at a rate of five mm/min by symmetrically moving the two barriers placed on opposite sides of the trough. This rate was chosen such the system had enough time to re-equilibrate after the changes in area.

In experiments where imaging was used, the entire Langmuir-Blodgett trough was placed under the EP3 Imaging ellipsometer, which was manufactured by NanoFilm Ltd. The entire apparatus sits on an optical table to minimize the effect of vibrations. The images themselves were taken with a charge-coupled device under a 10x objective lens using a 532 nm incident light. Two sets of images are presented for each measurement—one is in standard black-and-white the other is in false-color red. This is done, as sometimes morphological features are more apparent within

one set than the other. Because the same objective was used every time, the scale for all the Brewster angle microscopy pictures is uniform: 1.8 cm corresponds to 50 microns within the image. Lastly, in a few pictures, mostly the ones taken in the presence of colloids, the gain was adjusted downwards because of undue brightness within the picture. Care must be taken in comparing different images, as a specific morphological feature or pattern that is bright within one image may be dimmer within another.

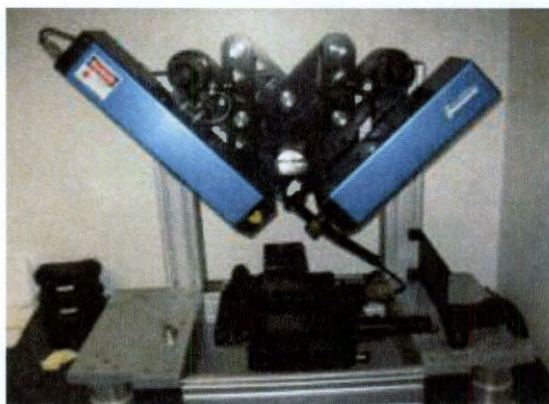


Figure 6: EP3 ellipsometer for imaging systems of colloids and polymers

Lastly, it is important to mention the wave-like patterns emanating from the bottom-left hand corner that appear within the BAM images. This is due to the incident light diffracting at the interface. Fortunately, there is image processing software available that is native to the EP3 software which corrects for this unavoidable background. A baseline image is fed into the ellipsometry software for a period of twenty to thirty seconds. Any future images taken by the software will automatically subtract this baseline image, as well as smooth out the brightness. It is only after this baseline image is taken that any material is added to the trough. In

this manner, any specific morphological patterns of interest that ultimately arise from our experiments are not excluded from the final image.

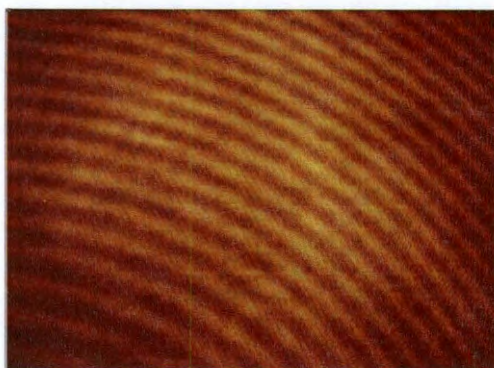


Figure 7: Background or "control" image of the Langmuir-Blodgett trough



Figure 8: Sample image after the background has been removed by the image processing software

3.2 Experimental Data and Discussion

We first begin by examining the pressure (π) versus area (A) isotherms of pure PLA. For the PLA, ($R_g = 63$ nm), we discovered a plateau at around 11 mN/m. The presence, as well as the surface pressure, of this plateau persisted regardless of compression rate, or initial amount of polymer deposited to the air/water interface. This matched well with data taken previously by Amini in his research on PLA monolayers, as well as data that had been previously published by Esker et al. Although the surface pressure did not agree exactly with Esker's work, this is probably due to the gross difference in molecular weights between the PLA used within our experiments and Esker's. We believe both of these plateaus correspond to the structural phase transition from the liquid-expanded, isotropic phase to the liquid-condensed, smectic phase.

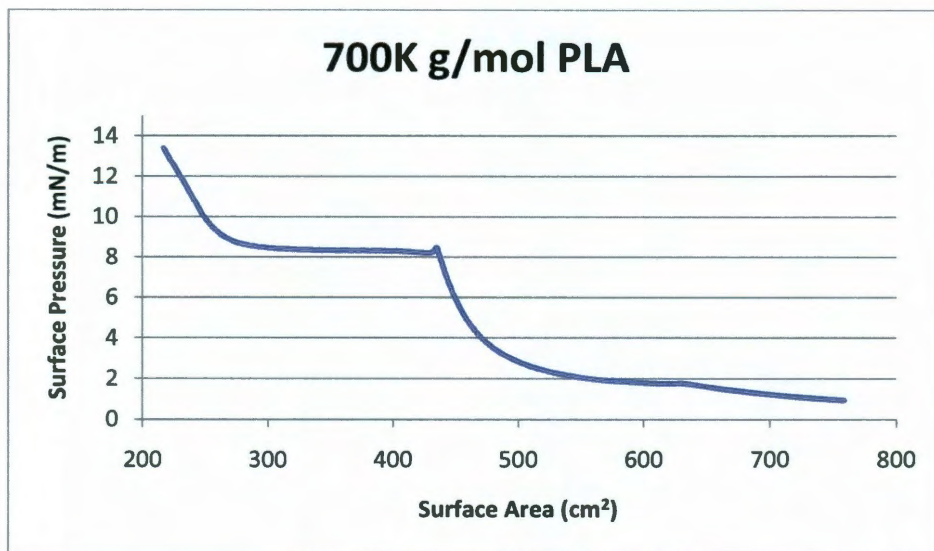


Figure 9 : Surface pressure vs. area isotherm for 63 nm PLA. The surface pressure corresponding to the plateau is 11.766 nM/m

We also examined the pressure (π) versus area (A) isotherms of pure colloids. The air/water interface on the Langmuir-Blodgett trough was cleaned and the colloids were deposited onto the interface in an identical manner to the poly-lactic acid, and were allowed to also sit for fifteen minutes in order to allow the chloroform to evaporate before any experimentation began. The results from these experiments also matched well with the data taken by Amini. We did not observe any discernable phase transitions for samples of pure colloids, up and through monolayer collapse and multilayer formation. Although in theory, a plateau should occur during, or before the formation of multilayers due to the fact that solidification is indeed a phase transition, however, this plateau was not seen due to the finite size of the instrument; in other words, any further compression would have resulted in the barriers on the Langmuir-Blodgett trough striking and damaging

the Wilhelmy plate. Although it may have been possible to experimentally observe this liquid-to-solid transition through increasing the amount of colloid initially added to the Langmuir-Blodgett trough.

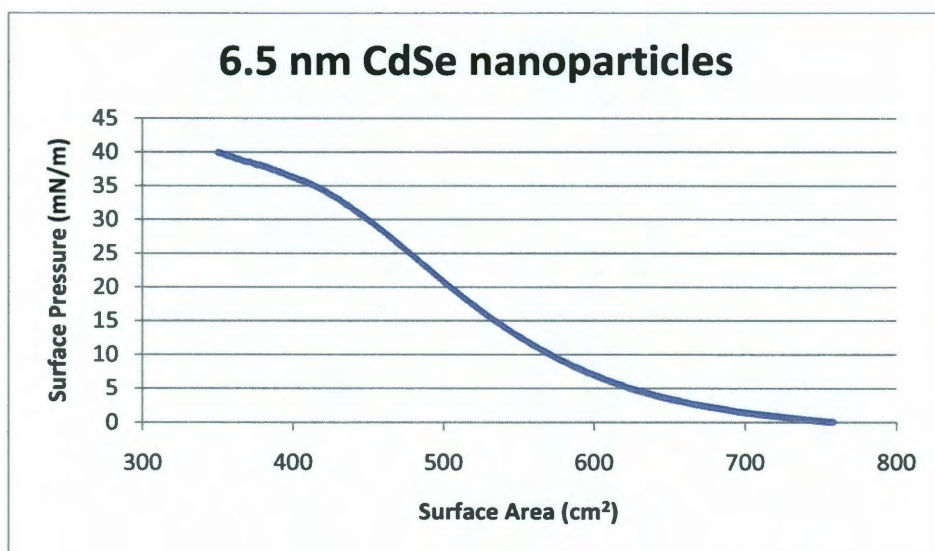


Figure 10: Surface oressure vs. area isotherm for 6.5 nm CdSe nanoparticles.

Significant imaging work using Brewster Angle Microscopy was also done on these isotherms in order to more specifically study the morphology and microstructures of the phase transitions of colloids and polymers. It is important to note that these imaging experiments are merely an extension of the Langmuir-Blodgett isotherm experiments in that the exact same experimental technique and setup are used. The only disparity is that the entire setup now rests under an imaging ellipsometer. Two major differences exist when taking microscopy measures. The first is the minimum size the Langmuir-Blodgett trough can reach, and the second is the speed at which the compression can occur. High compression rates (above 5 mm/min) will result in poor image quality due to mechanical

vibrations caused by the gears moving the barriers. Also, the location of the goniometer with respect to the barriers on the trough prevents compression below 200 cm^2 . Below 200 cm^2 , the barriers will strike the goniometer and cause damage to the ellipsometry unit. Fortunately, most morphological features of interest are independent of compression rate, and occur between 600 cm^2 to 350 cm^2 . As a result, these two constraints imposed by the ellipsometry unit do not affect the final outcome of the experiments.

Below are images obtained from a Brewster Angle microscopy experiment on pure PLA, along with the accompanying Langmuir-Blodgett isotherm that was generated while the pictures were taken.

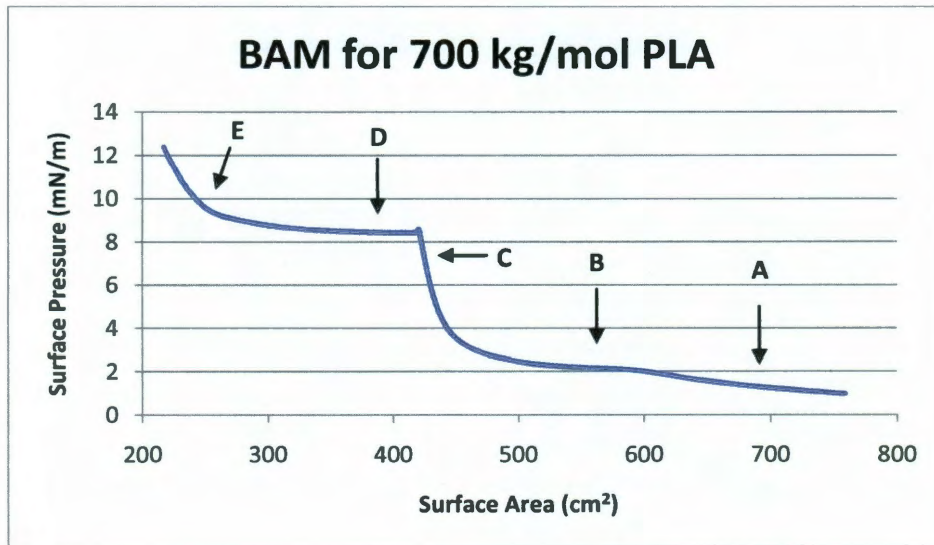


Figure 11: Surface pressure vs. area isotherm accompanying figures 11 to 15.

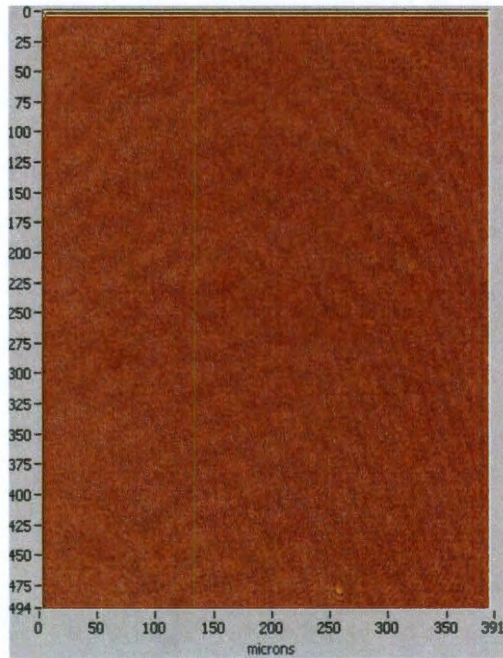


Figure 12: Brewster angle microscopy image at location A, shown in Figure 10

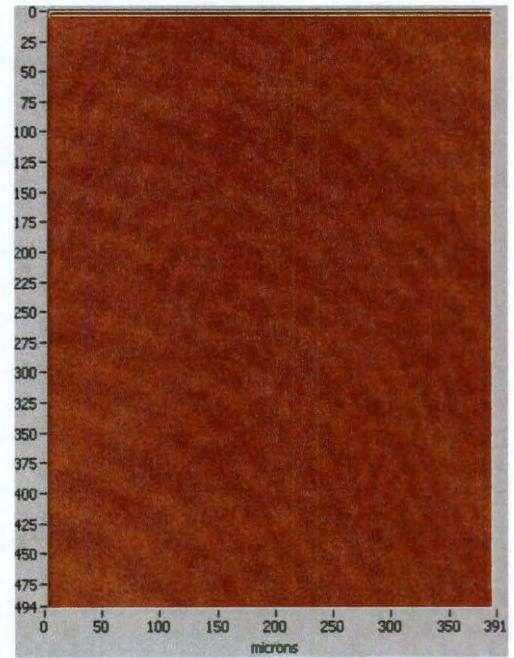


Figure 13: Brewster angle microscopy image at location B, shown in Figure 10



Figure 14: Brewster angle microscopy image at location C, shown in Figure 10

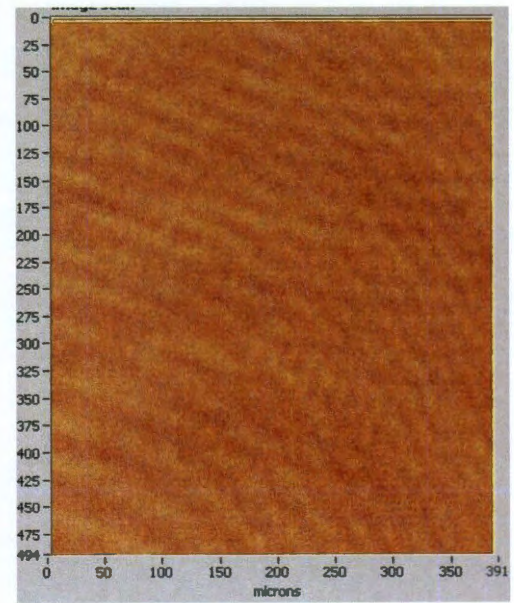


Figure 15: Brewster angle microscopy image at location D, shown in Figure 10



Figure 16: Brewster angle microscopy image at location E, shown in Figure 10

When examining the pictures, one must remember that the diffraction of the incident laser causes wave-like patterns emanating from the lower left hand corner of the picture, as described above. Although this has been corrected, to some extent, by the image processor built into the ellipsometry software, unfortunately not all traces of it can be eliminated. However, despite this, we can make a few key observations. First and foremost, the images become brighter and brighter as the surface area decreases and the surface pressure increases. This is indicative of a film being present on the air/water interface, rather than sinking down into the subphase below. In the absence of a film, an increase in surface pressure would not lead to a brighter surface.

Another important key is the propagation of the white islets as the system is being compressed and the orderly pattern they take on. We believe these white islets are indicative of the liquid-expanded to liquid-condensed phase change as mentioned by Esker et al., as their presence becomes more and more pronounced at regions close to, and after, the plateau. Qualitatively, they appear to form orderly patterns that are indicative of a smectic phase as seen in some liquid crystals (Ni, Lee, et al. 2006), however this is impossible to verify without the use of more sophisticated microscopy techniques such as AFM or SEM, as we cannot get the required nanoscale-resolution required to make such conclusions.

These imaging experiments were also repeated for pure colloids. Below are images obtained from a similar experiment done on pure colloids, along with the accompanying Langmuir-Blodgett isotherm that was generated while the pictures were taken.

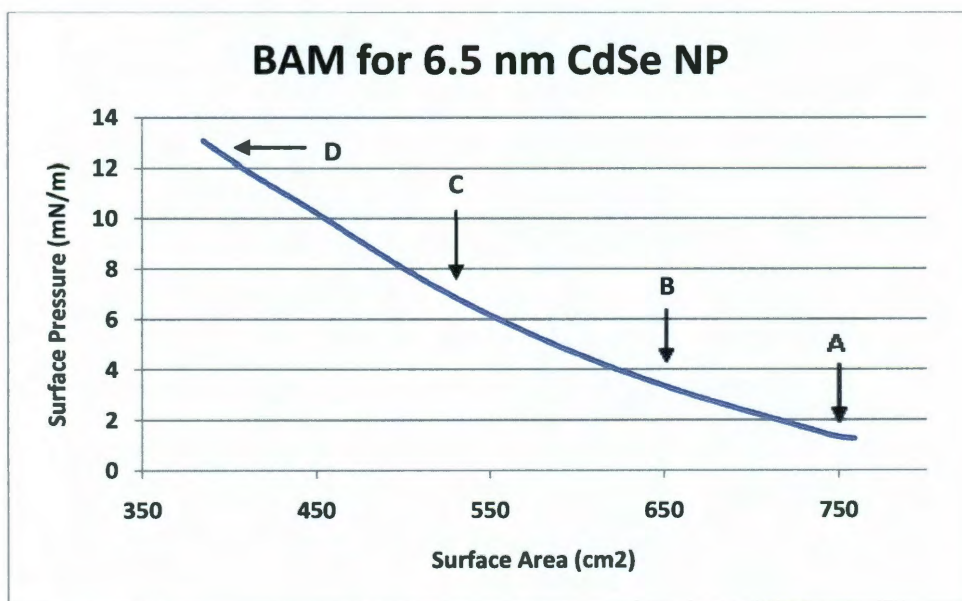


Figure 17: Surface pressure vs. area isotherm accompanying Figures 17 through 20

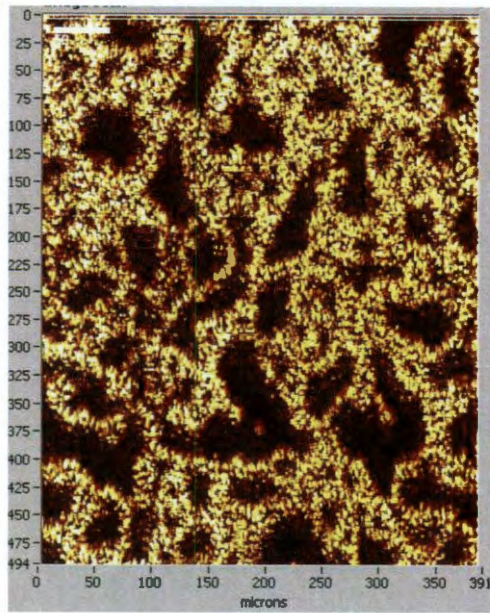


Figure 18: Brewster angle microscopy image at location A, shown in Figure 16.

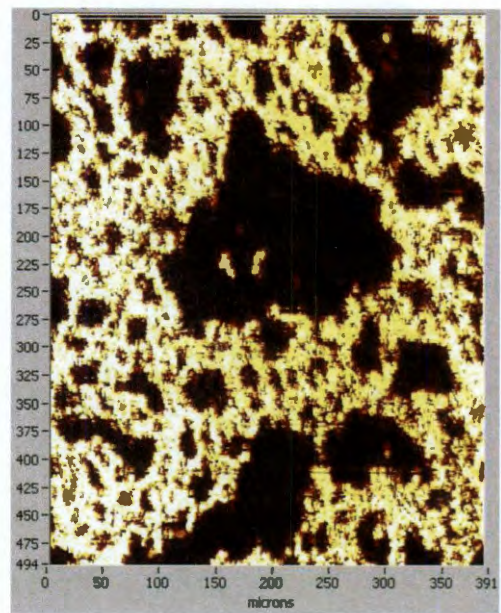


Figure 19: Brewster angle microscopy image at location B, shown in Figure 16.

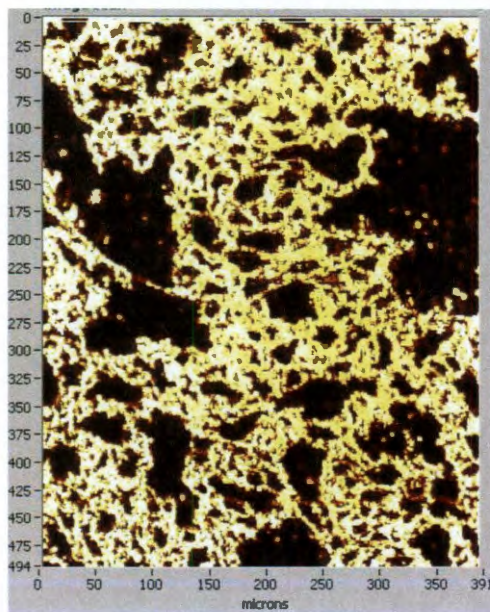


Figure 20: Brewster angle microscopy image at location C, shown in Figure 16.

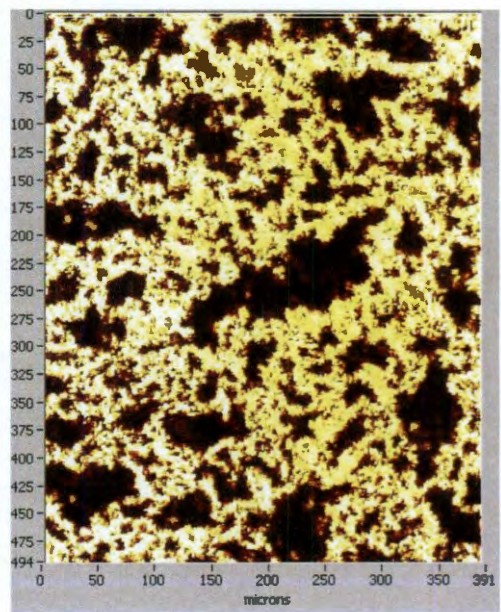


Figure 21: Brewster angle microscopy image at location D, shown in Figure 16.

We were, at first, rather surprised at these images, as we did not expect that these nanoparticles would agglomerate to this extent. At first, we believed that the CdSe nanoparticles were flocculating in the bulk before deposition on the Langmuir-Blodgett trough. However, an extensive DLVO calculation suggested that these nanoparticles were stable in the bulk, as the eighteen-carbon long ligand chain was sufficient to provide steric stability. Furthermore, a dynamic light scattering experiment showed that there was no large-scale aggregation in the bulk, as the mass majority (well over 90%) of the colloids were around 6.5 nm, as per the manufacturer's claims. Despite both theoretical and experimental proof, these images seemed contradictory, as it appeared as if the colloids were aggregating, to some extent, before compression. Indeed, increasing the system pressure only made the aggregation worse, as at the end, only a collage of entwined colloids remained. This was readily seen in the bulk too, as a thin film was floating on the air/water interface that could have been easily scooped up with a spatula upon conclusion of the experiment. Believing high concentrations to be the problem, we reduced the initial amount of CdSe nanoparticles added by 10-fold and repeated the experiment.

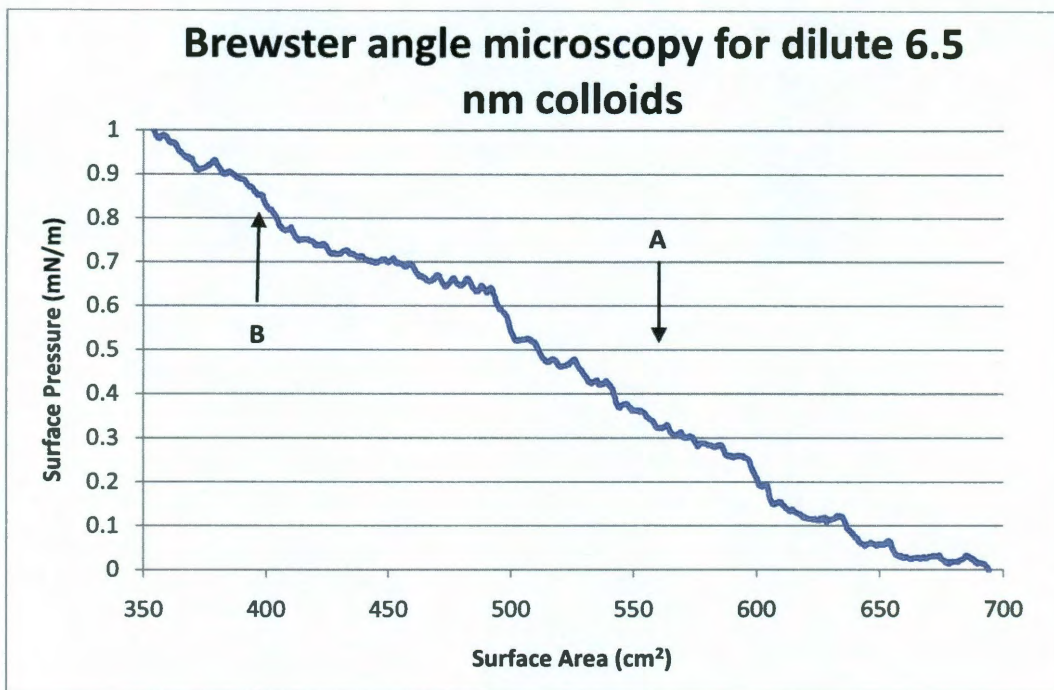


Figure 22: Surface pressure vs. area measurements accompanying Figures 22 and 23.

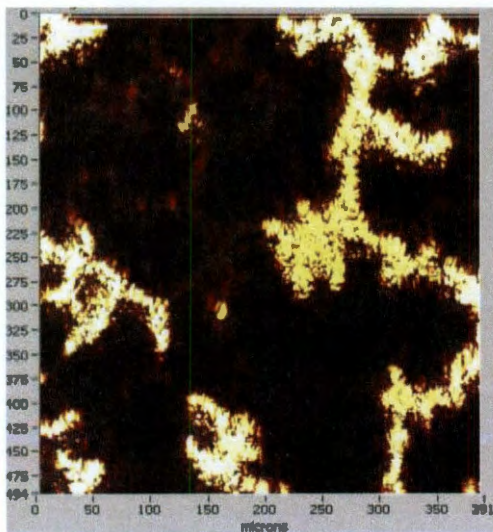


Figure 23: Brewster angle microscopy image at location A, shown in Figure 21.

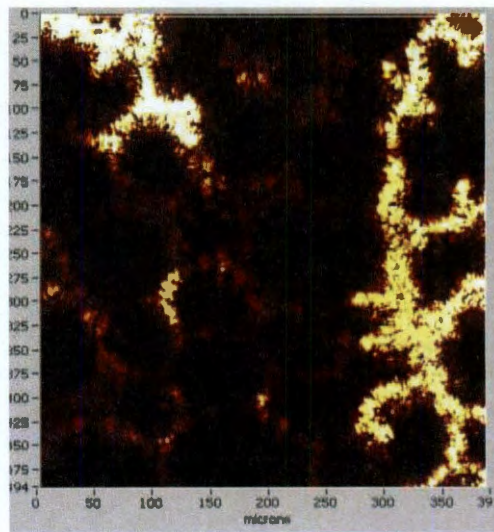


Figure 24: Brewster angle microscopy image at location B, shown in Figure 21.

After reducing the initial concentration of colloids added by tenfold, we still saw a significant amount of flocculation occur. What was more surprising was the formation of dark circular and hexagonal patterns, as seen in Figures 22 and 23. As the samples became compressed, these circular regions would progressively become lighter and lighter, until they formed elongated, branching shapes, as can be seen on the right of Figure 23, that were already indicative of flocculation. The mechanism for this transition between dark, hexagonal structures and brightly elongated shapes, was not clear to us until Schwartz proffered his comments. Schwartz believes that the highly hydrophobic nature of the colloidal ligands (hexadecylamine) causes the CdSe nanoparticles to immediately flocculate upon contact with water, and form a foam, as apparent in the dark, hexagonal structures. Further compression induces the colloids to form an elongated structure, of which the mechanism may be guided by diffusion-limited aggregation. These observations explain why bulk aggregation only appeared when the CdSe nanoparticles were added to the Langmuir-Blodgett trough, and were not seen in the bulk.

Chapter 4: Future Research

An important next step for this research is to examine the effect of different stabilizing ligands on the colloids. The 6.5 nm CdSe colloids were stabilized with octadecylamine – a highly hydrophobic surfactant, due to its highly apolar nature. However, it may be useful to study the effect of a less polar surfactant such as sodium dodecyl sulfate (Figure 25: Chemical structure of) or ammonium lauryl sulfate (Figure 26: Chemical structure of). The extra oxygen groups allow for a more polar or a more hydrophilic character when compared with octadecylamine, therefore, should not flocculate to the same extent upon contact with water. A minor concern is that SDS or ALS may not be long enough to sterically stabilize the colloids. This is easily remedied, as one can synthesize a surfactant with a longer carbon chain that precedes the polar end group (*e.g.*, sodium octadecyl amine). Although doing so will increase the ligand's overall hydrophobic character, the sulfate end-group will interact with the water via hydrogen bonding and prevent such an immediate and strong hydrophobic response that led to flocculation as seen when octadecylamine was used as the stabilizing ligand – even at such low colloidal concentrations.

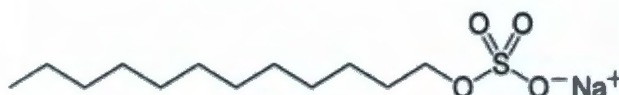


Figure 25: Chemical structure of sodium dodecyl sulfate (SDS)

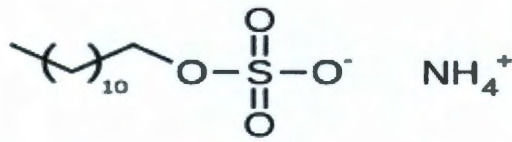


Figure 26: Chemical structure of ammonium lauryl sulfate (ALS)

First and foremost, one has to ensure that the polymer does not interact with the colloid; thermodynamically speaking, this must mean the enthalpy of mixing between the polymer and the colloids must be negligible. This must be ensured because repulsion or attraction between the colloids and the polymer may be enough to induce a phase transition. Furthermore, it is not enough that the colloids and the polymers do not sense each other – to be absolutely rigorous, one must ensure that the ligands which sterically stabilize the colloids also do not interact with the polymers, as a repulsion or attraction in this case may also lead to a phase transition.

Buoyancy effects must also be carefully considered when studying mixtures of colloid and polymers. Because our mixtures sit upon an aqueous subphase, it should be expected that the colloids will sit at a different horizontal plane compared to the polymers due to buoyancy forces arising from the innate differences in density between them. As a result, when a homogeneous mixture of polymers and colloids is compressed on a Langmuir-Blodgett trough, a situation may arise such that the polymer passes over the colloids and there is no interaction between them at all; this becomes an especially serious concern in the case where one of the components is qualitatively very small, either in absolute size, or in comparison to the other component. Care must be taken while verifying these results via experiment to ensure that both the colloids and the polymer lie on the same horizontal planes.

Lastly, it is important to mention briefly the dearth of mesoparticles available for commercial purchase. While colloidal particles of radius below 10 nm or above 1-micron can be readily purchased, there are none commercially available for purchase in the 50 nm to 500 nm size regime that is suitable for our experimentation purposes. Note that any colloidal particles, whether purchased or synthesized, must be resistant to dissolving in inorganics such as chloroform or methylpyrrolidone, as well as have negligible surface charge. A possible solution may be to synthesize silica colloids via hydrolysis of tetraethyl orthosilicate (TEOS) in the presence of ethanol. The size of the silica colloids can then be varied by changing temperature, the amount of ethanol, and the initial concentration of TEOS. Ligands such as SDS or ALS can then be covalently bonded to these silica colloids for the purposes of steric stabilization. Light scattering experiments must then be performed afterwards to ensure monodispersity. This process is perhaps the most feasible method of producing colloids of the proper size in order to perform experiments involving mixtures of polymers and colloids.

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