

THE PENNSYLVANIA STATE UNIVERSITY
SCHREYER HONORS COLLEGE

DEPARTMENT OF CHEMICAL ENGINEERING

CREATING POLLOIDS – A SYNTHESIS OF COLLOIDAL POLYMER CHAINS

CHARLES ALLEN MICHAELIS
SPRING 2013

A thesis
submitted in partial fulfillment
of the requirements
for a baccalaureate degree
in Chemical Engineering
with honors in Chemical Engineering

Reviewed and approved* by the following:

Darrell Velegol
Distinguished Professor of Chemical Engineering
Thesis Supervisor and Honors Advisor

Michael Janik
Associate Professor of Chemical Engineering
Faculty Reader

* Signatures are on file in the Schreyer Honors College.

ABSTRACT

Colloidal particles have been used to study atomic and molecular systems for over a century. Using physically deformed micron-size polystyrene latex particles, chains of colloids were fabricated, taking advantage of electrostatically repulsive surface functionalization and attractive van der Waal forces. These chains, ranging from a few particles to as many as 35 particles, were observed to follow known polymer theory, even showing hyper branched polymer systems. The chains are self-assembling and flexible, and hold promise in fields such as viscoelastic lubricants, biomimetic functional structures, and fluids with enhanced thermal conductivity.

TABLE OF CONTENTS

List of Figures	iii
Acknowledgements	iv
Chapter 1 Introduction	1
Chapter 2 Background	3
Flattening Colloidal Particles	3
Creating Colloidal Doublets	5
Chapter 3 Experimental Methods	9
Flattening Polystyrene Latex Particles	9
Stimulating Doublet and Chain Flocculation	10
Confocal Microscope Sample Preparation	11
Scanning Electron Microscopy	11
Sucrose Density Matching	11
Chapter 4 Results	12
Chapter 5 Conclusion	18
REFERENCES	19

LIST OF FIGURES

- Figure 1¹ – three stages of flattening are shown. (a) Particles are electrostatically adhered to the glass substrate, induced by the positively charged amidine surface chemistry of the particle and negatively charged silicon groups in the glass. (b) The particle is exposed to high temperatures (~120 °C), allowing surface tension to pull and deform particle on substrate. (c) The particle is cooled and scraped off of the substrate. To the right is SEM image of flattened particles.4
- Figure 2² – A plot of secondary energy minimum vs. the Debye length. The Debye length is related to the charge nonuniformity near the surface of the particle due to surface charge. This directly relates to the ionic strength of the solution. The Debye lengths shown corresponds to a salt concentration between 1 and 50 mM KCl, a larger Debye length referring to a lower salt concentration. As seen from the verticle lines, the middle region shows strong flat-flat interactions (thick green line) while maintaining weak interactions for flat-round (dotted red) and round-round (thin purple).....7
- Figure 3³ – Polloids follow classical polymer theory for condensation polymerization (a) SEM image of flattened APSL particles. (b) Confocal Microscope image of polloids created in 20 mM KCl solution. The bond strength is weakest, creating shorter chains. (c) Confocal Microscope image of polloids in 25 mM KCl solution. These chains are longer than in (b) because the inter-colloidal attractive force is stronger. (d) Confocal Microscope picture of polloids in 30 mM solution. These chains are long due to strong flat-flat and flat-round interactions. The Salt concentration is still low enough to prevent round-round interaction and clumping of particles. (e) Plot showing most-probable distribution, of N , the number of particles, vs. p , the number of flats in flat-round bonds. Fitted p lines are shown. The inset graph shows maximum at $N = 7 \pm 1$ for most probable weight fraction distribution in linear condensation polymerization in the highest concentration polloids system.14
- Figure 4³- Secondary Energy Minimum vs. Concentration of KCl. The plot shows the increases in secondary energy minimum value as salt concentration increases. As salt concentration increases, the Debye length decreases, decreasing repulsive forces and allowing stronger interaction between particles. As shown by the dotted lines, between 25 and 30 mM KCl flat-round interactions are strong (15-17 kT), while round-round interactions are still weak (< 10 kT).....15

ACKNOWLEDGEMENTS

I would like to recognize Dr. Laura Ramirez for her guidance and support through this research. Her leadership and vision for the project were invaluable. I would also like to recognize Dr. Darrell Velegol for his advising of the project and his oversight on this thesis. In addition to these, I would like to thank all those who worked on the project before me, as well as Dr. Michael Janik for his input and help with this thesis.

Chapter 1

Introduction

Colloidal particles systems have been used to model atomic and molecular systems for over a hundred years. Some of the first research in this area was conducted relating to Brownian motion, the random movement of particles suspended in a liquid or gas. This motion was believed to be caused by the impact of these particles with atoms; if Brownian motion could be confirmed, then it would also indirectly prove the existence of these atoms and molecules that were impacting the movement of visible particles. Colloidal particles seen under the microscope could be tracked and studied, eventually leading to the confirmation of Brownian motion and indirect proof of atoms and molecules.

The advantage of using colloidal particles for atomic research is twofold; the particles are observable in the visible light range, allowing use of optical microscopes, and they behave and interact on a timescale that is also observable, on the order of seconds and minutes as opposed to fempto- or microseconds. If a micron sized system can be created that simulates molecular systems, many different experiments could be performed to expand and confirm polymer theory. Several efforts have been made toward this end. Some systems have been designed to use “lock and key” bonding selectivity and depletion forces, DNA-functionalized colloidal particles that link through base pairing, and integrating polymer molecules with metal nanoparticles^{4,6,5}. Using the earlier work of Ramirez et al., we will look at the use of flattened colloidal particles to create colloidal chains to simulate molecular polymer systems. The flattened particles allow selective bonding due to increase interaction areas. By controlling how the particles interact, through the ionic strength of the solution, they can be assembled into hyper-branched chains. Ultimately, the

question is this – does the ionic concentration in the system affect the degree to which flattened colloidal particles assemble into chain systems?

Chapter 2

Background

This thesis is the last step of several years' work and two published papers by Dr. Laura Ramirez et al. The original goal of the work was to create colloidal particle chains using double-flattened particles and inducing interaction using depletion forces. While the original methods were not the path used, the ultimate goal of creating flexible “polloids” (colloid polymers) was achieved. Several other groups have worked toward a similar goal using different means, but this method provides superior chain lengths and properties.

Flattening Colloidal Particles

The first step in creating colloidal chains is creating anisotropic (directionally dependent) colloidal particles. Some previous process included heterogeneous chemistries, having regions of different surface chemistry on each particle. Some others have used physical deformation, but it is much less common. Ramirez et al. developed a method for creating a flat patch on the particles, which would allow a region of increased interaction between particles.

The flattening process suggested in the first paper by Dr. Ramirez is relatively simple – the particles are electrostatically adhered to a glass substrate, they are exposed to a high temperature to allow deformation, and then are cooled to keep their shape. Through regulating temperature and time of exposure, flat sizes can be controlled, and desired deformed particles can be produced.

When the particles are heated above their glass-transition temperature (T_g), they become soft and malleable. This allows surface tension forces between the particle surface and the glass substrate to deform the particle, making a flat patch in the region between the particle and glass. Thorough modeling and experiments determined that this process scales with $t^{1/3}$. Figure 1 shows the basic 3 steps of the process.

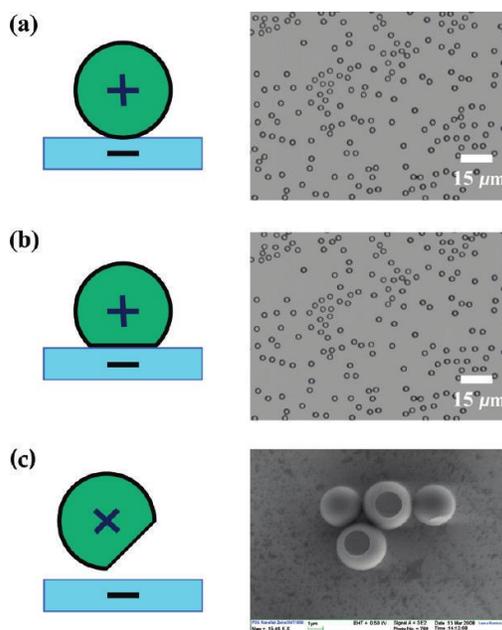


Figure 1¹ – three stages of flattening are shown. (a) Particles are electrostatically adhered to the glass substrate, induced by the positively charged amidine surface chemistry of the particle and negatively charged silicon groups in the glass. (b) The particle is exposed to high temperatures (~ 120 °C), allowing surface tension to pull and deform particle on substrate. (c) The particle is cooled and scraped off of the substrate. To the right is SEM image of flattened particles.

While this flattening process worked, two main problems were encountered when making the flats. First, high temperatures caused a chemical reaction at the amidine groups on the surface of the particles. The functional groups would undergo hydrolysis, replacing the amidine groups with carboxyl groups. Carboxyl groups have a negative charge – causing several problems. The particles would become either neutrally (half carboxyl and half amidine) or negatively charged. The neutral particles would now be able to aggregate due to van der Waals forces, and negatively charged particles would not adhere to the substrate. Secondly, the particles would not settle evenly on the surface of the glass, causing particles that were too close to merge together during

the flattening process. This not only decreased the number of flat particles, but also caused problems when trying to create doublets and chains.

The solution to each problem was found by Dr. Ramirez, and is described in her paper. The first problem was to eliminate the necessity of heating the particles, while also allowing them to become soft for flattening. The answer was to not heat the particle above the T_g , but to lower the T_g to room temperature to allow flattening at STP. This was induced by introducing a plasticizer, specifically toluene, to the flattening process. The particles were now able to be flattened without denaturing their surface chemistry.

The uneven settling of the particles on the glass was found to be caused by leaching of ionic species from the glass. This induced regions of different charges, causing the particles to settle in clumps on the surface. The solution was to settle particles on silicon wafers, not glass. The negatively charged surface chemistry was still present, but without the leaching ions from the surface. The substrate switch allowed very even spreading and settling of the particles. Now that a consistent process for creating flattened particles had been established, the goal of creating bonds between them could now be pursued.

Creating Colloidal Doublets

The APSL (amidine polystyrene latex) particles have two fundamental forces acting between units – electrostatic forces and van der Waals forces. Electrostatic repulsion between the particles, induced by the positive amidine functionalization on the surface, counteracts the attractive van der Waals forces. In normal suspensions, the electrostatic repulsion is desired to keep the colloidal suspension stable and dispersed. By controlling the strength of the electrostatic force, strong, reversible bonds can be created between particles.

DLVO modeling of colloidal particle interactions takes two inter-particle forces into consideration; the electrostatic repulsive forces and van der Waals attractive forces. DLVO, named after Derjaguin and Landau, Verwey and Overbeek, is a guide to theoretically determining the stability of the colloidal systems⁹. Evaluation of the DLVO models produce curves that show pairwise interaction energies for two particles. With modification by Ramirez, models were developed to determine interactions between different geometric configurations of particles, specifically trying to determine an ionic concentration at which flat-flat interactions are strong, while flat-round and round-round interactions are weak.

The ionic concentration of the solution specifically controls the Debye length, the distance over which ions screen out electrostatic forces. The Debye length (κ^{-1}) is defined by:

$$\kappa = \left(\frac{2z^2 n_{\infty} e^2}{\epsilon kT} \right)^{0.5}$$

where the valence $z = 1$ for KCl, n_{∞} is the bulk ionic concentration, e is the proton electric charge, and ϵ is the permittivity of the water². Under normal conditions, $\sim .1$ mM KCl, this length is 30 nm, and does not greatly impact the electrostatic repulsion of the particles. This keeps the particles stable in solution, not aggregating due to van der Waal's forces. But if the ionic concentration is increased, the Dybye length increases, masking the electrostatic repulsion and allowing van der Waals forces to "bond" the particles together.

Flat-flat bonds are able to selectively be made because they have a larger surface area of interaction. When two unflattened particles approach each other, they are only able to closely interact with a very small portion of each other's surfaces. By introducing a flat region on the particle, the two particles are able to interact more like two flat plates. This increased area of interaction causes a larger magnitude of interactions. By selecting an appropriate salt concentration, based on DLVO theory and Debye length calculations, and thus particle interaction strength, the flat-flat bonds can be strong while the round-round bonds can be weak.

Quantitatively, a strong interaction is on the order of 25 kT (a measure of energy on the molecular scale, k is Boltzmann's constant and T is absolute temperature), while a weak interaction is considered to be less than 5 kT . It is important to note that these energies refer to a second energy minimum interaction. At the second energy minimum, there is a strong inter-particle attraction, but there is still a gap of water between the colloids. This layer is important because it allows flexibility and reversibility of binding. If the ionic concentration was increased sufficiently, the particles would enter the first energy minimum, where the van der Waals forces significantly overpower electrostatic repulsion and the particles are more rigidly bound and actually contact each other. Figure 2 shows the Debye length (a value dependent on salt concentration) vs. the secondary energy minimum. As shown by the vertical lines, there is a region in the middle where flat-flat interactions are strong while other interactions are still relatively weak².

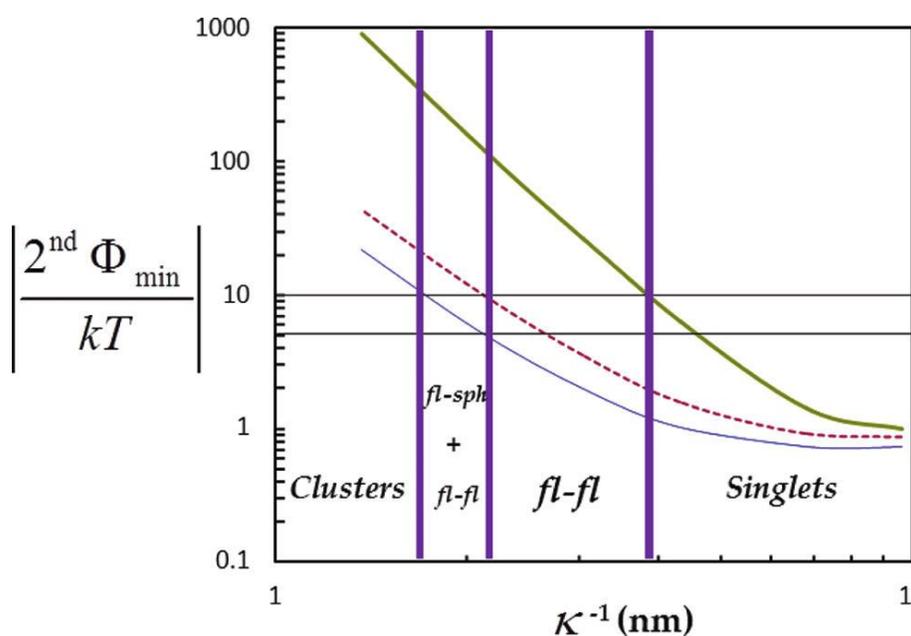


Figure 2² – A plot of secondary energy minimum vs. the Debye length. The Debye length is related to the charge nonuniformity near the surface of the particle due to surface charge. This directly relates to the ionic strength of the solution. The Debye lengths shown corresponds to a salt concentration between 1 and 50 mM KCl, a larger Debye length referring to a lower salt concentration. As seen from the vertical lines, the middle region shows strong flat-flat interactions (thick green line) while maintaining weak interactions for flat-round (dotted red) and round-round (thin purple).

The methods developed to flatten the particles and induce self-assembly into strongly bound doublets were necessary steps toward making colloidal chains. Although many difficult challenges had to be overcome, including many challenges with flattening the particles, studies could now move toward the end goal.

In this thesis, I examine how we can use flattened particles to create chains of colloids, or polloids. Specifically, does the concentration of ions in the solution affect the bonding strength and degree of polymerization of polloids? We hypothesize that as ionic strength increases from 20 to 30 mM KCl, the strength of flat-round and flat-flat bonds will become stronger and lead to polloid formation of longer and longer lengths, while round-round interactions will remain unfavorable, preventing unwanted aggregation of particles.

Chapter 3

Experimental Methods

Flattening Polystyrene Latex Particles

Polystyrene Latex particles of several sizes were used in the flattening process, ranging from 1 to 3.3 μm in diameter. The particles are monodisperse, surfactant-free amidine-functionalized polystyrene latex (APSL) microspheres (2.2 μm particles - particle density (ρ): 1.055 g cm^{-3} , average diameter (2a): 2.2 μm , coefficient of variation (CV):6.0 %, surface charge density (ρ_s):22.7 $\mu\text{C/cm}^2$, batch no:2681,1). All particles were purchased from Interfacial Dynamics Corporation (Portland, OR). First, small ($\sim 1 \text{ cm}^2$) pieces of silicon wafer were cut and submerged in DI water in plastic petri dishes. Then 15 μL of the particles was added to the dish and swirled to ensure homogeneous dispersion of the particles in solution. The dishes were then covered and placed in the refrigerator (to prevent denaturing of functional groups) overnight to allow the particles to settle and electrostatically adhere to the silicon wafers. The petri dishes were then washed with 150 mL of DI water to remove loose particles. The particle covered wafers were then transferred to plastic 50 mL beakers, where they were submerged to a depth of 7 mm in DI water. Next, 1 mL of toluene was added to the surface of the water and covered with parafilm. The wafers were then allowed to sit for between 1 and 4 hours, depending on ambient room temperature, allowing the toluene to diffuse through the water to the particles. The small amount of toluene allows the particles to viscously spread on the surface of the wafer. After the allotted time, the toluene is removed from the surface with a pipette, and the sample is rinsed with 500 mL of DI water. Then the sample is more thoroughly rinsed by a gravity flow system, passing 1 L of DI water over each wafer. This rinses the toluene from the polystyrene particles.

The particles are then scraped off of the wafers using a plastic pipette, transferred to Eppendorf tubes, and stored in the refrigerator. The particles are then further concentrated through centrifugation. For testing temperature effects on the toluene flattening process, samples were placed in an incubator or water bath at varying temperatures and times.

Stimulating Doublet and Chain Flocculation

The flattened APSL particles can be flocculated through the introduction of a salt concentration. Based on DLVO models developed by Ramirez et al., salt concentrations ranging from 20-30 mM KCl can induce flocculation to chain structures¹. 50 μL of flattened APSL particles are prepared in an Eppendorf tube. Then approximately 3 μL of 500 mM KCl is added to the solution of particles. The sample was vortexed for several seconds to ensure thorough mixing. Samples were then allowed to polymerize while rolling on a Penta KB Power Roller to avoid gravitational settling of the particles and chains. Flocculation took between 1 and 3 hours for each sample. Flocculation of doubles can be achieved through the same process, but lower salt concentrations (~ 10 mM) are used to prevent flat-round interaction.

Several different scenarios were set up and imaged. Flattened 2.2 μm particles were mixed with flattened 1 μm to make heterogeneous chains. 2.2 and 1 μm flattened particles were also mixed with 9 μm particles. Flattened 2.2 μm particles were also mixed with 3 μm magnetic particles for flexibility and bond strength experiments.

Confocal Microscope Sample Preparation

A sample of polloids was mixed with 1 mM Rhodamine B (a fluorescent dye) to be placed in a capillary 0.20 x 0.20 mm (VitroCom) and sealed with wax. Confocal images of settling polloids at different z-positions were taken with a Leica Microsystems TCS SP5 confocal laser scanning microscope (60x oil objective). Polloids were also imaged with a Nikon Eclipse TE2000-U inverted optical microscope (60x air objective).

Scanning Electron Microscopy

A scanning electron microscope (SEM) was used to image flattened particles to determine the flat sizes of the particles. Flattened particles were vortexed and sonicated to ensure dispersion, then allowed to settle and dry on a silicon wafer. The wafer was then gold plated and placed in the microscope for imaging. The images were then processed using Image J to determine particle and flat patch sizes.

Sucrose Density Matching

To enable imaging of particles and chains, solution density matching can be used to prevent settling of particles. Sucrose is added to DI water until the density is 1.055 g/mL, the same density of the APSL particles.

Chapter 4

Results

After the work conducted on creating doublet, the effort to expand these interactions into colloidal polymers, or polloids, could continue. To start, the original plan for fabrication of double flattened particles was tried. Using a similar method as making single flats, particles would be settled on silicon wafers, but this time the wafers would have v-grooves. In the groove, the particle would be able to flatten on two surfaces after being exposed to toluene. But this method proved difficult for two reasons; the particles did not settle well on the v-grooves, and the specially modified chips would be either very expensive (up to \$500 for a square centimeter of substrate) or long and laborious to fabricate. These difficulties led to a modification of the original plan.

With these difficulties, alternative methods were pursued. What if flat-round interactions could be made strong while keeping round-round bonds weak to avoid flocculation? When looking at figure 2, there are several regions of interaction. For making doublets, only flat-flat interactions were desired, induced by a salt concentration of 10 mM KCl. But, as shown in the region to the left of the only flat-flat strong bonds, there is a Debye length at which both flat-flat and flat-round interactions could be strong while round-round interactions were still relatively weak. Optimal conditions for forming these flat-round polloids could now be studied, as well as their properties relating to bond strength and flexibility.

Using figure 2 as a guide, specific conditions for creating polloids chains were pursued. Trying to create flat-round interactions without inducing round-round interactions proved to be a delicate process. To create strong bonds (> 15 kT) in the flat-round regime, salt concentrations

were required around 25 to 30 mM. In this range round-round interactions were <9 kT, but if the salt concentration was increase slightly (approximately 35 mM), the secondary energy minimum disappears and permanent aggregation of the particles is induced. The particles needed for these interactions have flat sizes that are greater than 50% of the diameter of the particle.

Figure 3 summarizes the effects of salt concentration on the formation of the polloids. Overall, as the salt concentration was increased from 20 to 30 mM KCl, chain lengths increased as well. At lower concentrations the shortest chains were observed, averaging 5 particles per polloid. This is because the secondary energy minimum is the smallest, making the bonds the least favorable of the salt concentrations. More doublets were observed because the flat-flat bonds were still strong (above 25 kT), while flat-round interactions were only around 10 kT. At 25 mM, the strength of the secondary energy minimum increases to approximately 14, and again increases to 17 kT at 30 mM KCl. These values can be seen in figure 4, which shows a plot of secondary energy minimum vs. concentration of KCl.

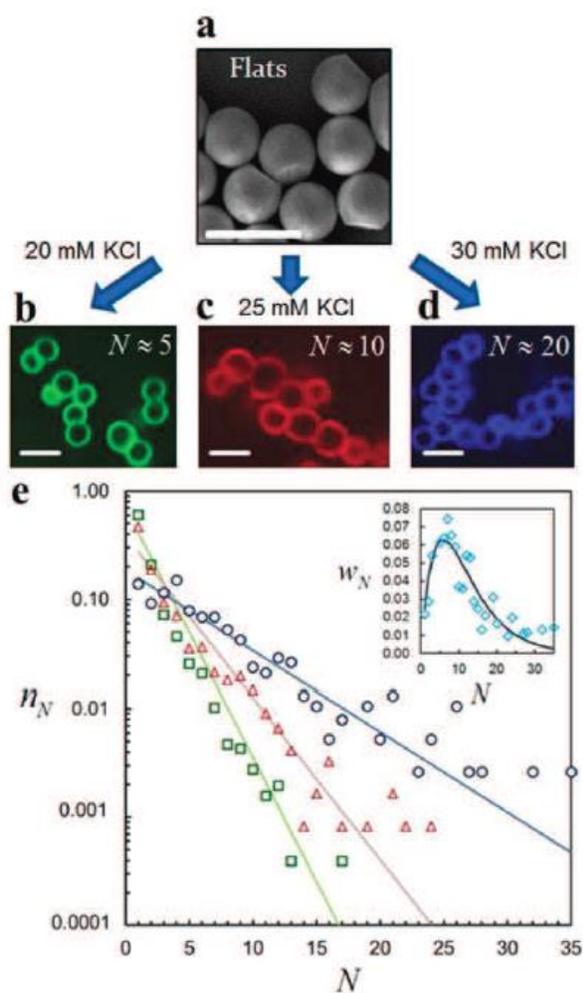


Figure 3³ – Polloids follow classical polymer theory for condensation polymerization (a) SEM image of flattened APSL particles. (b) Confocal Microscope image of polloids created in 20 mM KCl solution. The bond strength is weakest, creating shorter chains. (c) Confocal Microscope image of polloids in 25 mM KCl solution.

These chains are longer than in (b) because the inter-colloidal attractive force is stronger. (d) Confocal Microscope picture of polloids in 30 mM solution. These chains are long due to strong flat-flat and flat-round interactions. The Salt concentration is still low enough to prevent round-round interaction and clumping of particles. (e) Plot showing most-probable distribution, of N , the number of particles, vs. p , the number of flats in flat-round bonds. Fitted p lines are shown. The inset graph shows maximum at $N = 7 \pm 1$ for most probable weight fraction distribution in linear condensation polymerization in the highest concentration polloids system.

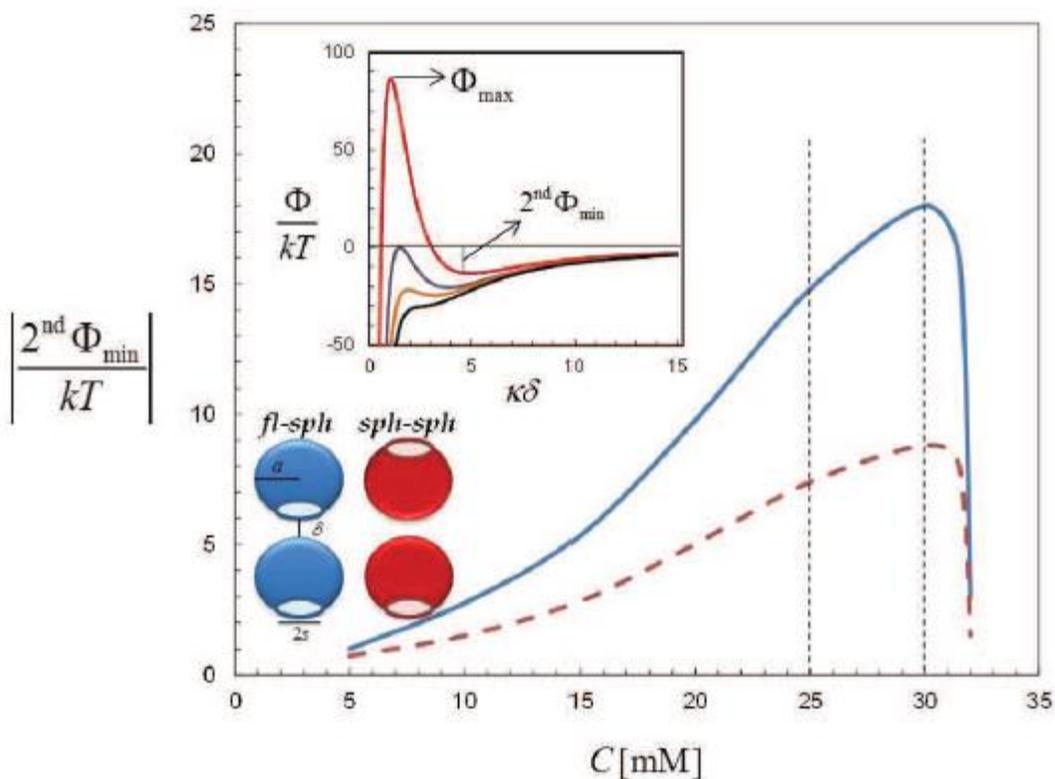


Figure 4³- Secondary Energy Minimum vs. Concentration of KCl. The plot shows the increases in secondary energy minimum value as salt concentration increases. As salt concentration increases, the Debye length decreases, decreasing repulsive forces and allowing stronger interaction between particles. As shown by the dotted lines, between 25 and 30 mM KCl flat-round interactions are strong (15-17 kT), while round-round interactions are still weak (< 10 kT).

Through controlling inter-particle forces with a low salt concentration, the flattened particles were successfully flocculated into colloidal polymers – polloids. These chains exhibited several valuable properties: they are flexible, due to the secondary energy minimum and a water layer between particles; they are hyper-branched, simulating a real polymer system; and they are reversibly bound – separation simply requires a decrease in salt concentration of the polloids suspension.

Chain flexibility was observed in several scenarios. First, by the nature of the system, particles settle out of solution onto the imaging substrate when using the optical microscope. Particle chains flatten onto the surface, allowing us to image and take statistics on chain lengths and particle aggregation. Then, assuming the particles are in 3-D conformations in solution, they

must flatten to match the 2-D substrate. This “flattening” can be observed when the microscope is focused on the substrate; as the chains settle, one end would appear, then more particles of the chain would come into focus, and eventually the whole chain has flattened out. Chain flexibility was also observed when mixing flattened APSL particles with magnetic particles. When they are mixed, the magnetic particles are included in the chains without flattening because flat-round interactions are strong in our system. Normal chain structures were observed (though naturally shorter because some of the particles are not flattened), and when a magnetic field was induced, the whole chains would move with the magnetic particles. The chains would move and flex to align the dipoles of the magnetic particles with the applied field, normally moving to a linear configuration from their random conformations, further showing flexibility in the inter-particle bonds. In addition to flexibility, this experiment also showed that the bonds between particles are also strong.

Inter-particle interaction strength was quantitatively studied using two methods – electrophoresis and applied magnetic fields. When a magnetic field was applied to the mixed particle systems, the chains not only moved with the magnetic field, but remained connected, even when the neodymium magnet was placed as close as possible to the particles. In several instances, the magnetic field would move chains slightly, causing new bonds to form. By moving the magnet, chains could be twisted and contorted. If a flat patch was exposed to another flat or a round section, it would move into the secondary energy minimum bond. After the connection was made, the bond could not be broken again by using the magnetic field to move the chains.

Using electrophoresis, the charged particles can be moved by applying an electric field across the imaging capillary. This action not only causes the particles and chains to move, but also exerts a force on the bonds. To allow for electrophoretic movement, the solution was density matched with sucrose, allowing the particles to be suspended in solution instead of settling on the substrate. After applying an electric field, the chains maintained their connections.

The flat-round colloids system allows for not only linear chains, but hyper-branched particle chains. Actual polymer systems exhibit hyper-branching, and thorough theory has been formulated on the subject. One measure of polymerization is f , the functionality, defined as the number of bonds per monomer. From analysis of images, this value was determined to be 2.01 ± 0.01 . Therefore, the colloids chains should resemble linear condensation polymerization ($f \approx 2$) closely³.

The particle chains follow classical polymer theory for condensation polymerization³, in this case having a functionality of 2. The most-probable distribution of molecules, or in our case APSL particles, is expressed by $n_N = p^{N-1}(1-p)$, where N is the number of “monomers” in the chain¹¹. Polymerization probability, p , is the fraction of flats that are connected in flat-round bonds. Figure 3 also shows this polymerization probability, and how it changes with salt concentration. At lower salt concentrations, 20 mM, which coincides with lower bond energy, ≈ 10.2 kT, $p = 0.59 \pm 0.04$, as yields chains from 2 – 15 particles long. With increased salt concentration at 25 mM, bond strength is ≈ 15.2 kT, and $p = 0.74 \pm 0.04$. Finally, flat-round interactions are strongest at 30 mM, ≈ 18.1 kT, yielding a high degree of polymerization, $p = 0.84 \pm 0.02$. The weight fraction, $w_N = Np^{N-1}(1-p)^2$, is shown in the inset of Figure 3. The graph, showing weight fraction at 30 mM, gives a maximum at $N = 7 \pm 1$, which is expected for linear condensation polymerization with $p = 0.86$. After analysis, these consistencies show that the flattened particle chains system simulates the properties of molecular polymer systems. The colloids system also gives the benefit of observing these “polymer systems, as the react and move on a visible length and time scale.

Chapter 5

Conclusion

In this thesis, we have developed a method for creating colloidal chains, that are flexible, reversibly bonded, and follow known polymerization theory. By using flattened micron sized polystyrene particles and manipulating inter-colloidal forces with salt concentration, we were able to control bond strengths and thus the characteristic lengths of the particle chains. At 30 mM KCl solution, long, hyper-branched polloids were observed, with as many as 35 particles in a flexible chain system. The system showed a p value of $0.86 \pm .02$, with a max weight fraction of $N = 7 \pm 1$. The chains were shown to be flexible, and strong, through both settling action and electromagnetic movement; they both stayed together during both processes, and easily conformed to the forces applied to them. Further research would include increasing production of flattened particles and polloids as well as perform rheological studies, specifically determining the viscous effects of dispersed and chained colloidal particles. The use of these chains can help further our understanding of molecular and polymer systems, having the distinct advantage of being on an observable length and time scale. Its application can impact fields from colloidal science to biotechnology to material sciences, and has the potential to expand or confirm the knowledge of systems that were previously not able to be studied in on an experimental level.

REFERENCES

- (1) Ramírez, L. M., Milner, S. T., Snyder, C. E., Colby, R. H. & Velegol, D. Controlled flats on spherical polymer colloids. *Langmuir* 26, 7644-7649 (2010).
- (2) Ramírez, L. M., Smith, A. S., Unal, D. B., Colby, R. H. & Velegol, D. Self-assembly of doublets from flattened spheres. *Langmuir* 28, 4086-4094 (2012).
- (3) Ramirez, L. M., Michaelis, C. A., Rosado, J. E., Pabón, E. K., Colby, R. H., Velegol, D. Polloidal Chains Composed of Flattened Particles. Under Review
- (4) Sacanna, S. W., Irvine, W. T. M., Chaikin, P. M. & Pine, D. J. Lock and key colloids. *Nature* 464, 575-578 (2010).
- (5) Liu, K. et al. Step-growth polymerization of inorganic nanoparticles. *Science* 329, 197-200 (2010).
- (6) Rogers, P. H. et al. Selective, controllable, and reversible aggregation of polystyrene latex microspheres via DNA hybridization. *Langmuir* 21, 5562–5569 (2005).
- (7) Li, D., Banon, S. & Biswal, S. L. Bending dynamics of DNA-linked colloidal particle chains. *Soft Matter* 6, 4197-4204 (2010).
- (8) Angioletti-Uberti, S., Mognetti, B. M. & Frenkel, D. Re-entrant melting as a design principle for DNA-coated colloids. *Nature Mater.* 11, 518-522 (2012).
- (9) Derjaguin, B. V. & Landau, L. D. Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solution of electrolytes.. *Acta Physicochim. USSR* 14, 633-662 (1941).
- (10) Verwey, E. J. W. & Overbeek, J. T. G. *Theory of the Stability of Lyophobic Colloids* (Elsevier Publishing Co., Amsterdam, 1948).
- (11) Rubinstein, M. & Colby, R. H. *Polymer Physics* (Oxford Univ. Press, New York, 2003).

ACADEMIC VITA

Charles Michaelis

3902 Pamay Dr. Mechanicsburg Pa 17050 camichaelis@comcast.net

Education

B.S., Chemical Engineering, 2013, The Pennsylvania State University, State College, Pa

Honors and Awards

- REU Research Grant for Summer 2012 from NSF – June 2012

Association Memberships/Activities

In this section, list all memberships in:

- American Institute of Chemical Engineers – student member

Research Experience

- Under Dr. Velegol and Dr. Ramirez, I worked on creating flexible, self-assembling colloidal chains through the introduction of flat patches and manipulation of inter-particle forces using salt concentrations.
- Under Dr. Hickner and Sean Nunez, I am working to create mix and pour recipes for ion exchange membranes for implementation in fuel cells and water purification processes.

Research Interests

My research interests lie in the future of energy for our nation and world. Specifically I have a passion for making current processes more efficient, such as more efficient cars or batteries, as well as developing new technologies, like solar power or fuel cells.