Synthesis of Rigid Colloidal Bead Chains in an Apolar Solvent

DUSTIN VAN WEERSEL [‡]

B. PENG: A. IMHOF
Debye Institute
Utrecht University

June 18, 2013

Abstract

When high frequency electric fields are applied to a system of colloids, they induce a dipole moment without changing the double layer surrounding the particles. This dipole moment drastically changes the morphology of the system by causing strong head-toe attractions and sideways repulsion, resulting in the formation of 1D strings, 2D sheets, and 3D crystals. By using a system comprised of a low concentration of spherical polymethylmethacrylate particles in an apolar solvent, bead chains form which can be made into permanent rigid strings by application of a heating step.

[‡] E-mail: D.A.G.vanweersel@students.uu.nl

Contents

1 Introduction 2
1.1 Colloids 2
1.2 Colloids under electric fields 2

2 Materials and Methods 3
2.1 Materials 3
2.2 Methods 4
2.3 Characterization of the particles 5

3 Results and Discussion 7
3.1 Preparing Electric Cells 8
3.2 Phase Behavior under an Electric Field 9
3.3 Comparing Two Systems of Different Particle Size 11

4 Summary and Outlook 14

5 Acknowledgements 14

1 Introduction

1.1 Colloids

The term *colloid* was coined by Thomas Graham in 1861 to classify particles which, when dissolved in an aqueous solution, would pass through parchment. One such material was glue, and the Greek word for glue is *kolla* from which colloid gets its name. Materials which did pass through parchment, like salt or other crystalline substances, were called *crystalloids.* Later it was observed that this definition of colloids was relative, due to the fact that it depends on the membrane if a material passed or not. Nowadays, several definitions exist for this state of matter. One widely used definition is *a particle between 1-1000 nm.* This class of particles is small enough to exhibit Brownian motion, but large enough to be studied with common optical techniques available to us. Examples of colloids are to be found in a variety of interesting substance which include, but are not limited to, milk, ink, blood, smoke, glue and asphalt.

1.2 Colloids under electric fields

An interesting phenomena occurs when colloids are exposed to high frequency AC-fields in a solvent that has a significantly different dielectric constant. The particles obtain a dipole moment and subsequently the macroscopic properties of the dispersion can change dramatically. One example is an increasing of the viscosity by several orders of magnitude which is used in industrial applications like hydraulic valves and displays. [1, 2] When observing colloidal systems under an AC-field, different interesting structures have been found. At low volume fractions strings formed along the direction of the electric field. [1, 2]. When higher volume fractions and stronger fields were present, 2D sheets and crystalline structures were found.

A recent method allows us to create permanent strings of colloids involving a heating step after application of an electric field. [3, 4] This facile method yields permanent strings with tunable stiffness in polar solvents that can serve as a colloidal analogue for polymers. In apolar solvents, only rigid strings can form.

2 Materials and Methods

Our method of fabrication follows the process outlined by B. Peng in ref:[4] involving two stages which omits the difficult to produce PHSA-*graft*-PMMA used in other production methods.[5] First monomer, stabilizer and initiator are present homogeneously in a medium. After heating the initiator decomposes, and the free radicals liberated start to react with monomers to form oligomer radicals. When a critical length is reached, the oligomers precipitate to form primary nuclei which absorb stabilizer on their surface. Fairly soon after the first nuclei appear, the monomer, dye monomer, and cross-linker will only be incorporated into existing particles and further nucleation stops. From this stage on, polymerization only occurs the swollen particles until all the monomer has been consumed. A fluorescent dye is added after the nucleation has finished to make the particles suitable for confocal microscopy.

For the creation of strings a high-frequency electric field (1 MHz) was applied, inducing a dipole moment which gives rise to head-to-head attraction and sideways repulsion.[2] This interaction, at low density, favors the formation of strings as opposed to other 2D and 3D structures. These strings can be thermally annealed to form permanent polymer bead chains.[1, 3, 4]

2.1 Materials

For the synthesis of particles, methanol and deionized water were used as solvents for the monomer methyl methacrylate (MMA, Aldrich). As stabilizer we used poly (vinylpyrrolidone) (PVP, K-90, Sigma) with an average molecular weight of 360,000 g/mol together with an initiator azobis-isobutyronitrile (AIBN, Janssen Chimica). Ethylene glycol dimethacrylate (EGDMA, Sigma-Aldrich) was used as the cross-linking agent. Finally (rhodamine B isothiocyanate)-aminostyrene (RAS) and ([2-(4-nitro-2,1,3-benzoxadiazol-7-yl)aminoethyl]trimethylammonium (NBD) were used as dyes to make the particles suitable for real space confocal microscopy study.

For the creation of strings cyclohexyl bromide (CHB, Sigma Aldrich) was used as a solvent, combined with the salt tetrabutylammonium bromide (TBAB, Sigma Aldrich) to decrease the Debye screening length. Two different batches of dried fluorescent labelled particles (RAS and NBD) of different sizes (0.8 µm and 3.2 µm in diameter) were used as our system. Two electric cells were created. For first cell a rectangular sample cell, a 0.1 mm × 1.0 mm capillary (VitroCom, U.K.), and 50 μm thick nickel alloy wires (GoodFellow, U.K.) were used.[3] For the second type of cell a non-conducting glass spacer with a thickness of 150 μm was used, together with two one side conducting glass plates. For details see the next section.

2.2 Methods

The solvent mixture used consisted of a 5:1 ratio of methanol and water containing 8.3 wt% PVP stabilizer. Two thirds of this mixture, 2.59 g of the monomer (MMA) and 0.025 g of the initiator (AIBN) were placed in a 250-ml, three necked flask equipped with a gas supply, a condenser, and a Teflon coated stirring bar. After a homogeneous solution had formed at room temperature, nitrogen was bubbled through the reaction system at room temperature for 30 min to deoxygenise the solution. After this, the flask was immersed in a silicon oil bath which maintained a temperature of 55°C and was stirred at 100 rpm. Following this 24.3 μL of the cross-linker EGDMA was dissolved into the remaining one third of the solution. After 1 hour his mixture was added to the reaction system dropwise at a constant rate with the aid of a peristaltic pump. After the addition was completed, the reaction system was maintained at 55°C for 24h before cooling. The final mixture was washed three times with methanol (Hettich Rotina 46 S centrifuge, at 315 g for 20 min) to remove the free stabilizer.

For the preparation of strings, two different types of cells were made ($\hat{y}$- and $\hat{z}$-cells) (see figure 1). In the first cell, the strings form in the $\hat{y}$ direction, and in the second they form in the $\hat{z}$ direction. The first rectangular sample cell consisted of a 0.1 mm × 1.0 mm capillary (VitroCom, U.K.) together with two 50 μm thick nickel alloy wires (GoodFellow, U.K.) threaded along the side walls.[3] The second cell was made using two thin glass plates which were conductive at one side. These were stacked upon each other with a spacer, after they were both connected with a 50 μm thick nickel alloy wires using glue and high concentration silver paint.

First, dried particles were dispersed in a mixture of CHB and tetrabutylammonium bromide (TBAB, Sigma Aldrich). The mass percentage of this mixture was about 1 wt%. Subsequently, the ends of the capillary were sealed off using no. 68 UV-curing optical adhesive (Norland) under an UV-lamp. After this a 320 V root-mean-square sinusoidal signal with a frequency of 1 MHz was applied for half an hour. After this the cell was heated for 7 minutes using a stream of hot air (70-75°) that was much wider than the

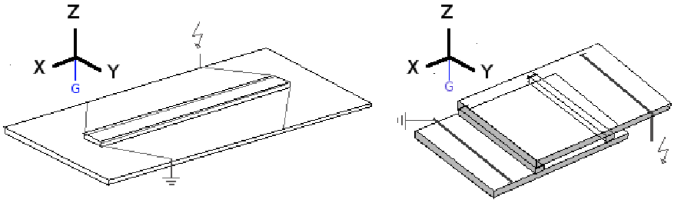

Figure 1: Schematic drawing of the $\hat{y}$- and $\hat{z}$-cell respectively

sample cell to thermally anneal the strings. After this cell was allowed to cool off and the electric field was turned off.

2.3 Characterization of the particles

The size and polydispersity of the PMMA particles were measured using static Light Scattering (SLS) (see figure 2). For this we took a highly dilute suspension in methanol and used home-built equipment equipped with a He-Ne laser as a light source (632.8 nm, 10 mW). Because methanol is a bad solvent, the particles did not swell. The scattering intensity was plotted against the scattering vector $k = 4\pi n \sin(\theta/2)/\lambda$, with n being the refractive index of the solvent, θ the scattering angle and λ the wavelength in vacuum. These curves were compared to theoretical ones obtained through simulation using Mie-theory for the scattering form factor for (polydisperse) particles with a core-shell or a homogeneous structure. The gaps between the peaks correlate to the size, and the depth of the curve relates to the polydispersity

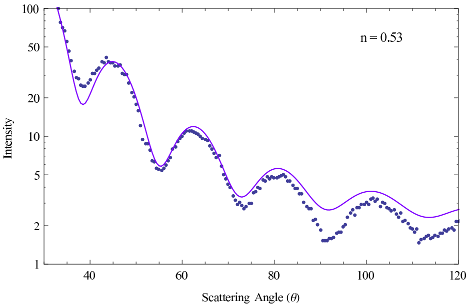

Figure 2: Theoretical curves plotted with the measured data.

We also measured the size and polydispersity using confocal microscopy, where we took an image of at least 300 particles which were attached to the walls of the cell and averaged over 4 images. Then the size was measured using the free software program ImageJ (see figure 3) and the polydispersity was calculated from this measurement. The polydispersity was defined as $\delta = \sigma/R$. The difference between the SLS and confocal measurement was determined and used to calculate the swelling ratio, defined as $\alpha = R_s/R_o$.

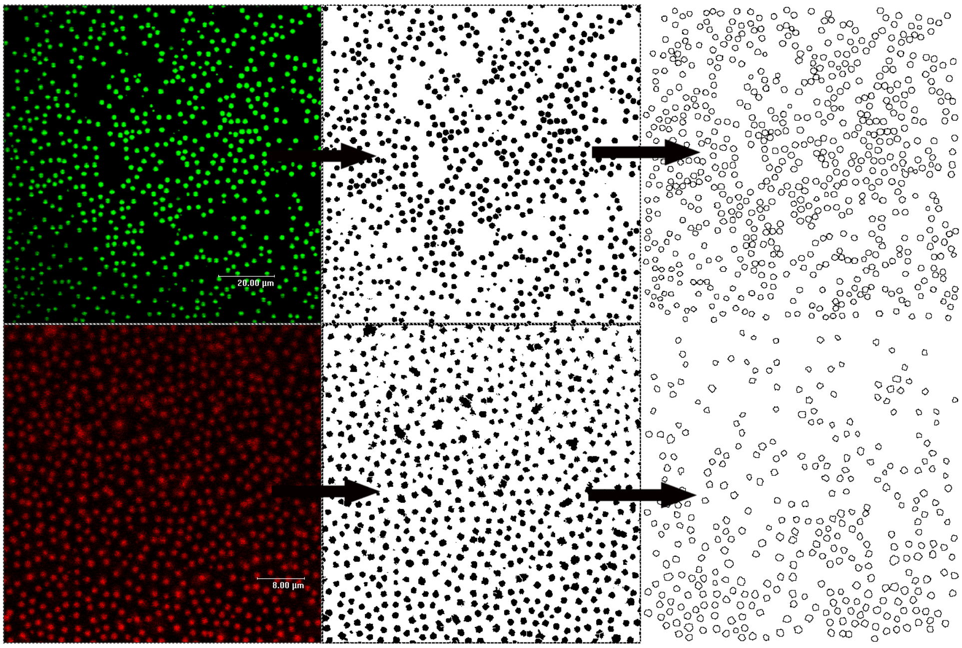

Figure 3: Automatic process of particle size measurement through ImageJ. First the image is converted to a greyscale and a threshold is applied to binarize the image. Then an automatic function within ImageJ is used with suitable parameters (minimum and maximum size and sphericity), that calculates the mean area and standard deviation, which is then converted to the radius and standard deviation of the radius.

To determine the morphology of the particles, confocal scanning laser microscopy (CSLM) was used to observe the fluorescently dyed particles, giving us a way for an in-situ real space study. For this a Leica confocal scanning laser scan head (Leica SP2) was operated in fluorescent mode on a Leica (DM IRB) inverted microscope. Measurements were performed with a Leica 63 × oil confocal immersion lens with a numerical aperture of 1.4. The fluorecently dyed particles were excited at around 543 nm (RAS) and 488 nm (NBD) and their images were observed at emission wavelengths of around 605 nm (RAS) and 515 nm (NBD).

3 Results and Discussion

Monodisperse fluorescent particles were made successfully and unlocked particles were used to create short stiff bead chains in an apolar solvent. Short branched strings were observed for the locked particles. Subsequent tries for locked particles in both type of cells were unsuccessful and produced a gel-like state. We observed a change in interaction strength and accordingly the formation of strings when the particle sized varied. Before elaborating our results, we will first give a concise description of dispersion polymerization.

Dispersion polymerization is a common method for creating micron sized, mono-disperse colloids and excels in creating high molecular weight polymers with fast polymerization rates. Often dispersion polymerization involves a solvent, monomer, stabilizing polymer, and a surfactant. For this process to work, the solvent of choice has to be a good solvent for the monomer, stabilizer and initiator. The resulting polymer, however, needs to be non-soluble in the solvent so it is separable. Lastly, the stabilizing polymer needs to have a higher affinity towards the polymer surface than the solvent. [6, 7]

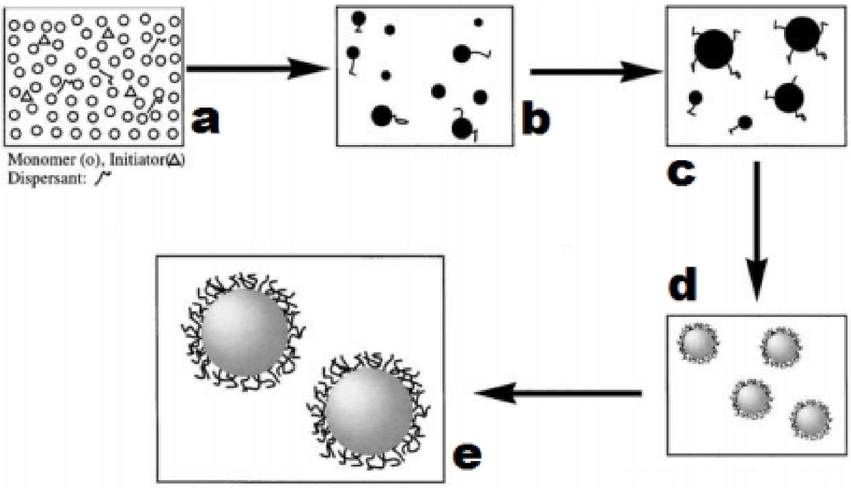

Figure 4: Schematic drawing of the dispersion polymerization of polymer colloids [7]

After all the ingredients are mixed into a homogeneous solution, the solution is heated to decompose the initiator into radicals which lead to the formation of small oligomers of the monomer (see fig 4b). Once the size of an oligomer reaches a critical value, it precipitates out of the solution and coagulates with other oligomers (see fig 4c). This continues until the oligomers are prevented from coagulation through steric stabilization by the stabilizing polymer (see fig 4d). From this point, no new particles are formed and the existing particles grow in size by coagulation with oglimers and nuclei and by polymerization of the monomer from the continuous phase (see fig 4e).[6, 7]

An apolar solvent (CHB) was used in this experiment. In contrast to polar solvents like formamide, CHB does not easily decompose under the application of an electric field and subsequently higher field strengths for longer times could be used. The refractive index of PMMA is quite low, in comparison to a common material like polystyrene, resulting in a good index match. This facilitates the real space observation with confocal microscopy.

3.1 Preparing Electric Cells

One common problem in the study of colloidal particles in confocal microscopy is the sticking of particles to the glass capillaries 5. This phenomenon is caused by the build up of electric charges on the surface of the colloid and the subsequent attraction to the glass. Because free particles are required for the synthesis of strings we looked at some options to obtain capillaries filled with free particles from a low concentration of PMMA particles in an apolar solvent.

Different coating procedures were used (see table 1) involving the stabilizer PHSA and the particles as seen in figure 5. To coat a capillary, it was filled with a coating material and was subsequently blown out using a nitrogen stream until there was no fluid left inside. Two small capillaries were coated with each procedure and then filled with the fluorescently dyed particles (0.4 wt%). Subsequently they were sealed using glue and observed using confocal microscopy.

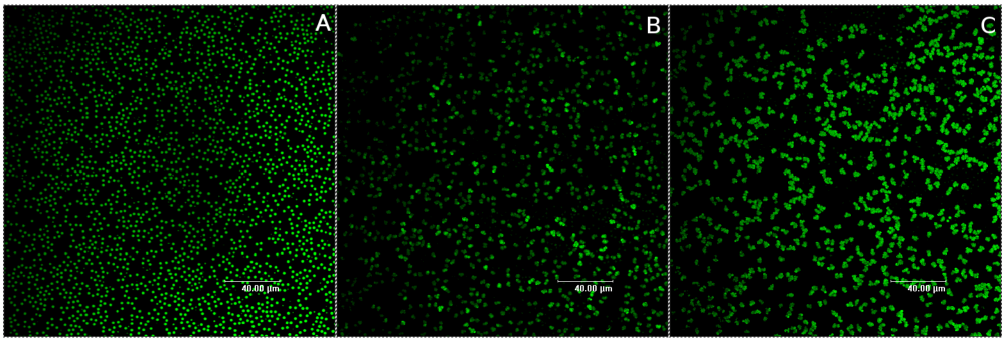

Figure 5: A: Glass wall filled with particles. B: 2 times coating for a short period, averaged over 15 seconds. C: 2x5 min PHSA coating averaged over 15 seconds

When only the stabilizer was used for a short time, little difference was seen. Giving the stabilizer time to connect with the walls provided some improvements. Coating with particles proved more fruitful, filling the walls and avoiding other particles to cream to the wall. One effect of the stabilizer we observed was the delayed (but eventual) sticking to the wall, explaining the mixed result of the third coating in table 1 due to the longer wait time between the samples.

-	PHSA	Particles	Capillary 1	Capillary 2
1	2x short	×	×	×
2	2x short	2x short	✓[1]	✓[1]
3	2x 5 min	×	✓	×
4	1x 10 min	×	×	×
5	2x 5 min [2]	×	✓[3]	✓[3]

Table 1: [1]High concentration of free particles. [2]The cell was reversed during the coating process.[3]Low concentration of free particles

3.2 Phase Behavior under an Electric Field

As stated, colloidal particles exhibit interesting interactions when a high-frequency electric field is applied. To describe the inter-particle interactions in our system of in a solvent which is refractive index matched we use the Yukawa pair potential approximation described in ref. [1], where

$$
\begin{aligned}
\frac{u_{Yukawa}(\mathbf{r}_{ij})}{k_BT} &= \begin{cases} \phi\frac{exp[-\kappa(\mathbf{r}_{ij}-\sigma)]}{\mathbf{r}_{ij}/\sigma} & \text{if } \mathbf{r}_{ij} \geq \sigma \\ \infty & \text{if } \mathbf{r}_{ij} < \sigma. \end{cases} \\
\text{with } \phi &= \frac{Z^2}{(1+\kappa\sigma/2)^2}, \\
\kappa &= \sqrt{8\pi\lambda_B c} \\
\text{and } \lambda_B &= \frac{e^2}{4\pi\epsilon_0\epsilon_m k_B T}
\end{aligned} \tag{1}
$$

With $\mathbf{r}_{ij}$ being the separation vector, k_B the Boltzmann factor, T the absolute temperature, σ the particle diameter, Z the particle charge, c the salt concentration, c the monovalent salt concentration, ϵ_0 the permittivity of vacuum and ϵ_m the dielectric constant of the solvent.

When the dielectric constant of the solvent is significantly different compared to that of the particles, and when an external AC electric field is applied the particles acquire a dipole moment. The induced inter-particle dipole interaction can be calculated using a point-dipole approximation. [1]

$$
\begin{aligned}
\frac{u_{dipole}(\mathbf{r}_{ij})}{k_BT} &= \frac{\gamma}{2}\left(\frac{\sigma}{|\mathbf{r}_{ij}|}\right)^3 (1-3\cos^2\theta_{ij}) \\
\text{with } \gamma &= \frac{p^2}{2\pi\epsilon_0\epsilon_m\sigma^3 k_B T} \\
p &= \frac{\pi}{2}\beta\epsilon_0\epsilon_m\sigma^3 E_{loc} \\
\beta &= \frac{\epsilon_p-\epsilon_m}{\epsilon_p+2\epsilon_m} \\
\text{and } E_{loc} &= E + E_{dip}
\end{aligned} \tag{2}
$$

Where $\mathbf{r}_{ij}$ the separation of the particles, θ_{ij} is the angle between r_{ij} and the field direction, ϵ_p is the dielectric constant of the particles, E is the external electric field, E_{dip} the induced dipole field and E_{loc} the local electric field.

From this formula it is clear that a greater difference between ϵ_p and ϵ_m produces a larger dipole moment p, resulting in a larger interaction of two particles. Also, a higher salt concentration induces a higher interaction and reduces the Debye length, giving rise to stronger inter-particle attractions. From eq.2 we can deduce that for $\theta_{ij} < 54.7°$ the interaction between particles is attractive and for $\theta_{ij} > 54.7°$ the attraction is repulsive. This causes the particles to align in strings along the field whilst avoiding sheets or other structures (see figure 6).

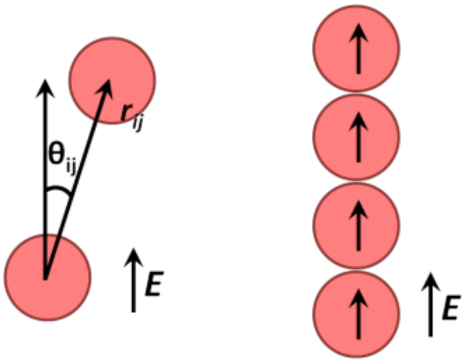

Figure 6: left:Two particles together with the separation vector and the angle θ_{ij}. right: A string of particles along the electric field [1]

When the size of the particles becomes smaller, the interaction between the particles becomes weaker. Smaller particles also exhibit larger diffusion, thus giving rise to forces that can break or disturb strings. From this we can conclude that strings will tend to form better in a system with larger particles at an equal field strength, in contrast to smaller particles.

3.3 Comparing Two Systems of Different Particle Size

We looked at two different batches of particles. Batch 1 consisted of unlocked NBD dyed particles with an average SLS measured diameter of 2.45 μm and a polydispersity of 3%. Confocal microscopy measurement gave a size of 3.2 μm and polydisersity of 2%. The second batch were locked particles dyed with RAS and with an SLS measured diameter of 1.1 μm and polydispersity of 4%. Confocal microscopy measurement gave a size of 1.3 μm and a polydisersity of 3%. From this data we get a swelling ratio of 1.3 and 1.2 respectively. For both systems, the solvent was a mixture of CHB saturated with tetrabutylammonium bromide and the resulting suspension of particles was around 1 wt%. The electric cells were coated twice with particles to give more free particles and to avoid later formed strings to attach to the walls. Before filling the particle suspension was dispersed using a handshaker (Retina Minishaker) for 5 minutes to disperse the creamed suspension because the particles and CHB are not density matched.

Batch 1 exhibited fast formation of strings (roughly 4-5 seconds) at 80 V/mm in both types of electric cells. At higher field strength and high densities, 2D sheets were formed with a hexagonal ordering in the $\hat{y}$-cells (see figure 7 A and B). At field strengths up to 320 Vm/m attempts to anneal the strings using a stream of hot air (70-75°) were unsuccessful (see figure 7C). The resulting suspension was filled with deformations, and a small amount of free particles were still present. When a longer heating step was applied of roughly 7 minutes, the strings became permanently fixed (see figure 7D andE, where E was the time averaged of the series D was taken from. The blurring in figure 7E is because of the movement of the strings. Unfortunately, due to the low occupation of particles at the wall these strings quickly became stuck and we were unable to study them further. When even longer heating steps were applied, the strings formed a rigid structure of combined strings with no definite ordering.

All strings that were observed were completely rigid. This can be explained by the low molecular weight of the stabilizer and the short range repulsions between the particles. After the heating step the stabilizers from both particles interconnect. However due to the short length of this stabilizer, not enough freedom is left for the strings to be flexible. Also, the short range repulsion between the particles is quite strong in comparison to the same system in a polar environment.

In contrast to batch 1, batch 2 formed strings a lot slower due to their smaller size. In the $\hat{y}$-cell at 140 V/mm short strings formed rapidly, and grew over time. For fields up to 320 V/mm attempts to anneal the strings were partly unsuccessful, producing bent and coagulated strings (see figure 8). Attempts with a 15 wt% suspension produced a gel-like state (figure 8B-D). In the $\hat{z}$-cells similar attempts, following the procedure outlined by H.R. Vutukuri [3] produced a similar gel-like state. Attempts to improve this result by applying heat over a longer time (10 minutes), slowly increasing the temperature for 3 minutes, using pure CHB to get stronger short range repulsion, and trying lower concentrations (7 wt%) also failed to reproduce the results.

One reason why permanent strings were made with unlocked particles and not with locked particles, perhaps comes from differences in the charge on the surface between the two particles.

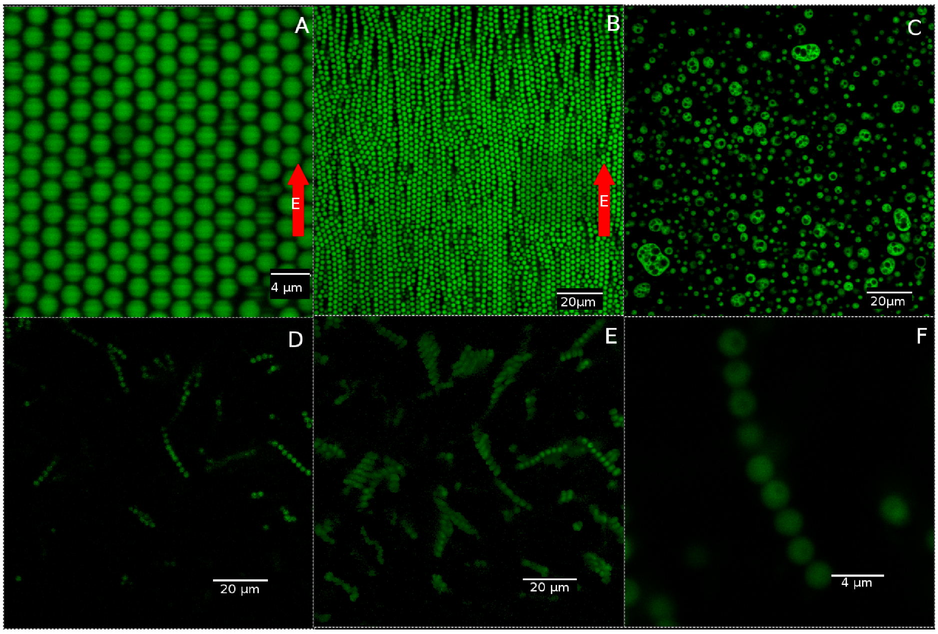

Figure 7: A: Closeup of the hexagonal ordering found in sheets B: Partially formed sheet-like structure C: Deformations after heating D: Rigid Strings E: Rigid strings averaged over 15 seconds F: Closeup and average over 15 seconds of a string attached to the wall

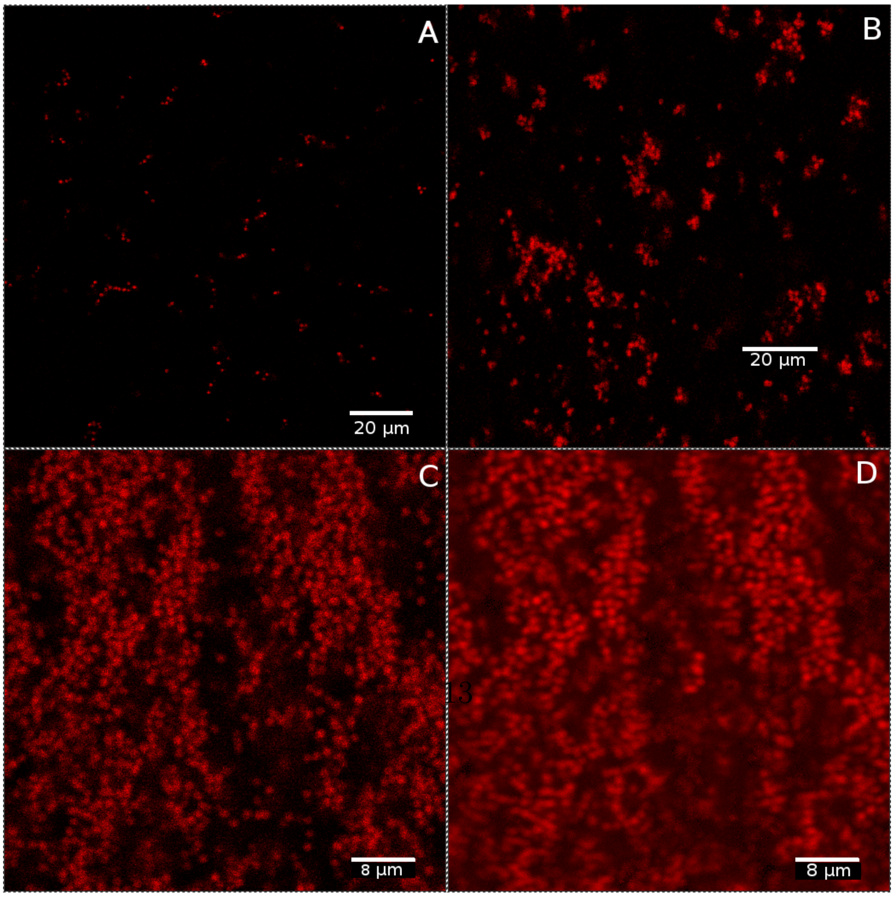

Figure 8: A: Small bended rigid strings B: Coagulations C: Gel-like structure after heating D: Gel-like structure averaged over 15 seconds.

4 Summary and Outlook

Concluding, we managed to synthesize mono-disperse spherical PMMA particles. Using a similar system of particles we were also able to produce permanent short strings in the system of larger unlocked particles and branched strings and gel-like structures in the system with smaller locked particles.

Improvements can be made on the comparison between the two systems by synthesizing one batch, and using subsequent treatments on a part of this batch to create dyed locked and unlocked particles. To further study the behavior of our rigid strings, tracking software can be used to track the dispersion of the strings. The effect of the size of the particles on the formation of strings can also be studied, giving an idea of the necessary field strength in relation to the particle size. Finally, a density matched mixture of *cis*-decalin and CHB [1] can be used to avoid creaming and give for an easier real space study of the formed strings.

5 Acknowledgements

I would like to thank Bo for his patience, guidance, and advice during the course of the experimentation and writing of this thesis. I would also like to thank Anne and Arnout for the helpful discussions and talks. Next to that I would like to thank Johan for the particles and everyone at the Soft Condensed Matter and Biophysics group for the coffee breaks, fun talks, and pleasant working environment.

References

[1] M. Leunissen. *Manipulating Colloids with Charges and Electric Fields.* PhD thesis, Utrecht University, 2007.

[2] A.P Hynninen. *Phase Behaviour of Charged Colloids and the Effect of External Fields.* PhD thesis, Utrecht University, 2005.

[3] H.R. Vutukiri, A. Demirors, B. Peng, P. van Oostrum, A. Imhof, and A. van Blaaderen. Colloidal analogues of charged and uncharged polymer chains with tunable stiffness. *Angew. Chem. Int. Ed.*, 2002.

[4] B. Peng. *Control over Colloidal Morphology by Dispersion Polymerization.* PhD thesis, Utrecht University, 2013.

[5] G. Bosma, C. Pathmamanoharan, E.H.A. de Hoog, W.K. Kegel, A. van Blaaderen, and H.N.W. Lekkerkerker. Preparation of monodisperse, fluorescent pmma-latex colloids by dispersion polymerization. *Journal of Colloid and Interface Science*, 2002.

[6] R.M. Fitch. *Polymer Colloids: A Comprehensive Introduction.* Academic Press, 1997.

[7] S. Kawaguchi and K. Ito. Dispersion polymerisation. *Advanced Polymer Science*, 2005.