

BACHELORTHESIS

# The Synthesis of Raspberry-like Particles Utilizing a Heterocoagulation Technique

De Synthese van Framboosachtige Deeltjes Met Behulp Van een  
Heterocoagultie Techniek



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## SUMMARY

Raspberry-like particles were made with spherical positively charged seed particles and spherical negatively charged smaller particles. The attraction from the small particles onto the surface of the seed particles is a heterocoagulation technique. It has been proven that it is essential that the seed particles contains poly-N-isopropylacrylamide (pNIPAM) for the attraction between the small particles and the large particles. The small particles make the surface of the raspberry-like particles rough.

The coverage (the amount small particles onto the surface of the seed particles) was varied through varying the salt concentration. It was confirmed that the coverage of the raspberry-like particle increases with increasing salt concentration. The analyzes were done with a transmission electron microscope (TEM) and with dynamic light scattering (DLS).

It has also been proven that the salt concentration can still influence the coverage after the forming of raspberry-like particles. This means that the dilutions before a measurement may not be performed with water. Water lowers the salt concentration and this decreases the coverage. This is the reason that the samples have to be diluted with a salt concentration where the raspberry-like particles are already in. Therefore, the raspberry-like particles keep the same environment and this gives more reliable results for the analyzes.

An optimal sequence exists for adding small particles, seed particles and salt together. This has to do with the moment **when** the small particles or seed particles comes in contact with a certain salt **concentration**.

## SAMENVATTING

Er zijn framboosachtige deeltjes gemaakt met sferische positief geladen kiemdeeltjes en sferische negatief geladen kleinere deeltjes. De attractie van de kleine deeltjes op het oppervlakte van de kiemdeeltjes wordt heterocoagulatie techniek genoemd. Er is gebleken dat het van essentieel belang is dat de kiemdeeltjes poly-N-isopropylacrylamide (pNIPAM) bevatten voor de attractie tussen de kleine en grote deeltjes. De kleinere deeltjes zorgen voor de ruwheid van het framboosachtige deeltje.

De dekking (hoeveelheid kleine deeltjes op de kiemdeeltjes) werd gevarieerd door de zout concentratie te variëren. Hiermee is bevestigd dat de dekking van het framboosachtig deeltje beter wordt, wanneer de zoutconcentratie toeneemt. Dit is geanalyseerd met een transmissie elektronen microscoop (TEM) en met dynamische licht verstrooiing (DLS).

Er is ook bewezen dat na de vorming van framboosachtige deeltjes de zoutconcentratie een invloed heeft. Dit houdt in dat de verdunningen (die uitgevoerd moeten worden voor een meting) niet met water verdund mogen worden. Dit zal de zoutconcentratie verlagen en hiermee de dekking verslechteren. Dit is de reden dat er verdund moet worden met de zoutconcentratie waar de framboosachtige deeltjes zich in bevinden. De framboosachtige deeltjes houden op deze manier dezelfde omgeving en dit levert voor de analyses een reëler resultaat op.

Voor het toevoegen van kleine deeltjes, kiemdeeltjes en zout bestaat een optimale volgorde, want er is bewezen dat een verschil in volgorde een verschil in dekking levert. Dit heeft te maken met **wanneer** de kleine deeltjes of kiemdeeltjes in aanraking komen met een bepaalde zout**concentratie**.



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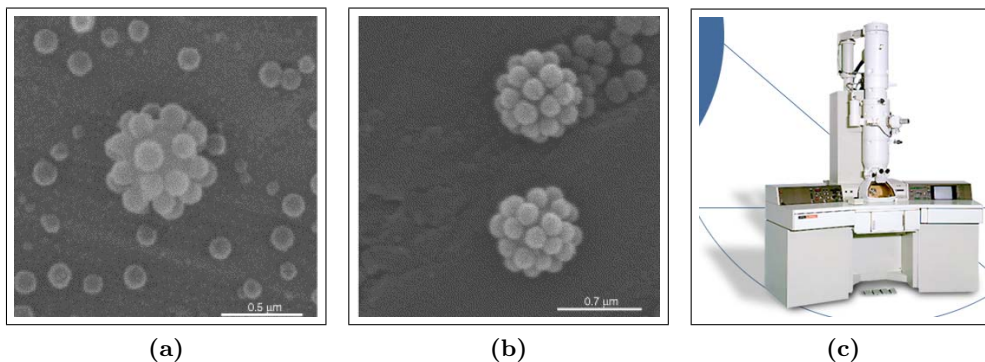
## Introduction

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There are many novel phenomena that occur on the nanoscale and that is why nanoparticles are very interesting. There is a wide range of nanoparticle types: dumbbells, core shell, cubes, rods, raspberry-like particles and even more. This thesis draws attention to particles with roughness on the surface. Such particles can be synthesized with different methods, for example with a heterocoagulation technique. The heterocoagulation technique of interest in this thesis is based on the attraction between bigger colloids (seeds) and smaller colloids. The small particles adsorb on the surface of the seed particles and make the particles rough. A particle with roughness on the surface is also called a raspberry-like particle (Figure 1.1a & Figure 1.1b).

A way to make raspberry-like particles is to synthesize small and large particles separately. These particles must be opposite of charge. Then, these particles can be mixed together and the smaller particles will adsorb on the surface of the seed particles. This is how raspberry-like particles can be formed. The coverage can be affected by adding an electrolyte solution<sup>[1]</sup>.

Another way to synthesize raspberry-like particles can be done with a polyelectrolyte. With this method, the seed particles and the small particles are both positively or negatively charged. Polymer chains can contain monomer segments with a certain charge. If this charge is opposite to that of the charge on the surface of the particles, the polymer chains will fold itself around the seed particles and the small particles will be attracted to the polymer chains. The polyelectrolyte serves as a sort glue to form raspberry-like particles<sup>[2]</sup>.



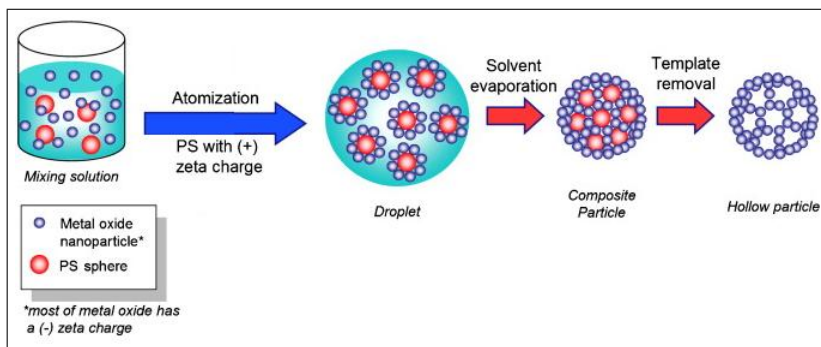
**Figure 1.1:** Figure (a) and figure (b) shows images of raspberry-like particles that are made with a Scanning Electron Microscope (SEM)<sup>[3]</sup>. Figure (c) shows a Transmission Electron Microscope (TEM)<sup>[4]</sup>.

These two methods are a small selection of all possible methods and these may be performed with different chemicals. Therefore, there are even more possibilities to synthesize raspberry-like particles. The particles can be analyzed on their raspberry-like shape by using an electron microscope (Figure 1.1c) and DLS.

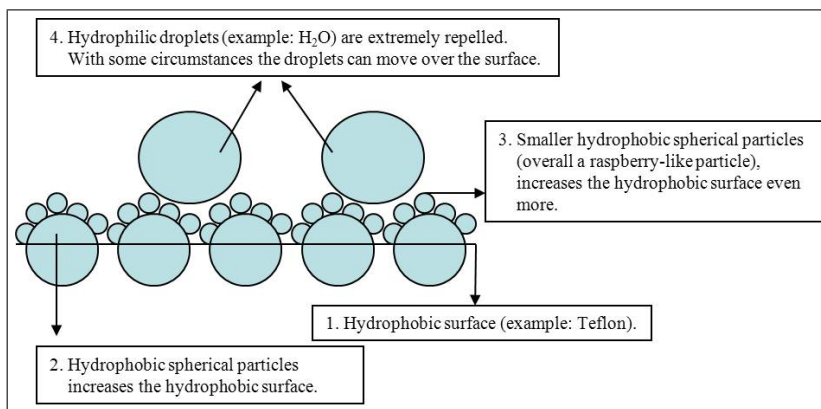
Raspberry-like particles can be used for novel phenomena like:

- **Hollow structure particles:** This kind of particles have the requirement that the seed particles are made from a different material than the small particles. This is because the seed particles will be removed after evaporating of the solvent (Fig 1.2a). These hollow particles are interesting for their excellent performance on bigger surface area, lower density and more. Therefore, hollow model particles have potential applications as catalysts, coatings, composite materials, fillers and so on<sup>[5]</sup>.
- **Wetting properties:** A surface can be increased by using raspberry-like particles. This is through their form. Due to this property, ultra hydrophobic material can be made. This is very interesting in the coating technology<sup>[2]</sup>. Figure 1.2b shows schematically how it works.
- **Roughness on the surface:** This is the phenomena of interest. It is about surface roughness induced self-assembly where the interparticle interactions depend on the roughness.

The goal for this thesis is to find out if raspberry-like particles can be made with polystyrene. Polystyrene is a commonly used polymer within the Physical & Colloid Chemistry group at the University of Utrecht. If this is possible it can be used for the phenomena "roughness on the surface".



(a)



(b)

**Figure 1.2:** Figure (a) shows schematically how hollow particles may be obtained. Figure (b) shows schematically how ultra hydrophobic material works.

## Chapter 2

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# Theory

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Before discussing the experiments, results, conclusions and discussions, the theory will be explained in this chapter. The theory is divided in different sections: The stability and synthesis of colloids, synthesis from literature, calculation for the coverage and analysis methods.

### 2.1 Colloids

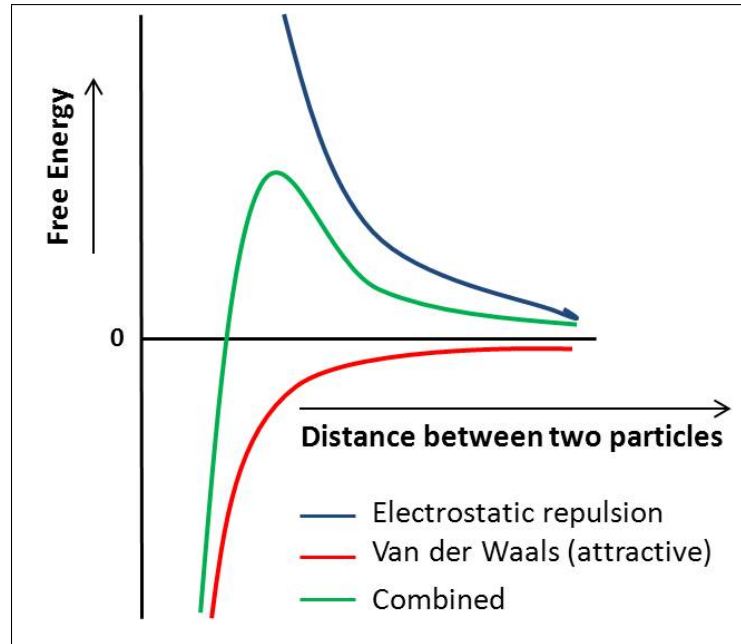
The particles discussed in this thesis are called colloids. Therefore, it is useful to know what colloids are. Everett<sup>[6]</sup> wrote a book about colloids and this book has been used for the study of it.

Colloids can have a variation in size from 10 to 1000 nanometers. The colloids in this thesis belongs to the dispersions that are synthesized by emulsion polymerization. A few examples of dispersions are:

- The phenomenon fog is a uniform distribution of little water droplets in the continue phase air (vapor).
- Milk has a uniform distribution of droplets fat in the continue phase water (emulsion).
- Paint has tiny solid particles distributed in a liquid phase (suspension).

#### 2.1.1 Stability

When the colloidal dispersion is formed, it is possible that the particles form aggregates. Under the influence of gravity this results in precipitation. The particles can aggregate because the free energy of two colloids decreases when the distance between the surfaces decreases. Because this is energetically favorable, there exists a spontaneous attraction force between two particles. But as mentioned before, the particles could be distributed uniformly in a dispersion. Therefore, a dispersion can have particles distributed uniformly in a dispersion (meta-stable equilibrium) or it can have particles aggregated out of the dispersion (stable equilibrium but it is no longer a dispersion). This is possible through the different forces that are present between the particles. When the distance between two colloidal particles is small, the particles will "feel" a lot of Van der Waals forces (attractive force). If the distance between the colloidal particles increases, the attractive force will decrease because it is proportional too  $\frac{1}{d^6}$  (where "d" stands for the distance between two particles). Repulsive forces are the forces that works against the Van der Waals forces. If the particles are both positively or negatively charged, the particles will repel each other (Coloumb's law), this is also called electrostatic repulsion. Another form of a repulsive force is steric stabilization. If the surface of particles contains relatively long polymer chains,



**Figure 2.1:** This figure shows schematically the attraction and repulsion forces between two colloidal particles.

the chains can hinder each other sterically and this is called steric stabilization. When the total repulsive forces is larger than the total attractive force, the colloidal dispersion shall be stable (Fig 2.1).

### Electrostatic repulsion

Electrostatic repulsion is a stabilization mechanism that was mentioned before<sup>[6]</sup>. To make use of electrostatic repulsion, a charge particle is needed. There are different methods to do this:

- Acid groups can be placed on the surfaces of the particles. When these groups dissociate, a negatively charged surface remains. This is identical for basic groups, where a positively charged surface remains. The strength of the charge on the surface can be influenced by varying the pH of the solvent.
- A partially soluble crystal will dissolve until the ion concentration is equal to the solubility of the crystal. When the solubility of positive ions is equal to the solubility of negative ions, the total charge will be zero. When the positive ions prefer to dissolve, a negative charge remains on the crystal.
- Active ions can adsorb on a surface. In the case of cationic surface active ions, the surface will become positively charged. For adsorbed anionic surface active ions the surface will become negatively charged.

When charged particles are obtained, the knowledge about fundamental electrostatic properties will be used to explain the effect of charges on colloids. However, first the effect of charges on ions will be discussed because this is more easily visualized. After that, the idea of the ions will be projected on colloids.

According to Coulomb's law, two ions ( $q_1$  en  $q_2$ ) with the same charge will repel each other and two ions with opposite charge will attract each other.

$$F = \frac{q_1 q_2}{4\pi\epsilon_0 d^2} \quad (2.1.1)$$

$F$  = The force between two ions (a positive value means repulsive force and a negative value means an attractive force).

$q$  = The electric charge of the ions (both positive or both negative results in a positive "F").

$d$  = The distance between two ions.

$\varepsilon_0$  = Dielectric constant of free space.

"In the presence of a material medium surrounding both charges, the force is reduced by a factor  $\varepsilon_r = \varepsilon/\varepsilon_0$ , the dielectric constant of the medium"<sup>[6]</sup>. The amount of work ( $W$ ) that is needed for bringing two charged particles together from infinite separation to a distance ' $d$ ' in a medium with dielectric constant  $\varepsilon$  is given with:

$$\Delta W = - \int_{\infty}^d F dh = \frac{q_1 q_2}{4d\pi\varepsilon} \quad (2.1.2)$$

The information so far tells something about the electrostatics of two ions but nothing about the electrolyte solution. To understand the influence of the electrolyte solution the Boltzmann's distribution law needs to be introduced. This law relates the probability of particles being at a given point with a certain potential energy, or free energy ( $\Delta G$ ), related to some chosen reference state. This can be expressed in terms of average concentration at a certain point:

$$c = c^o \exp \frac{-\Delta G}{kT} \quad (2.1.3)$$

$c^o$  = The concentration on the reference level where the energy equals zero.

$k$  = Boltzmann's constant.

$T$  = Temperature (Kelvin).

A relatively simple example is the distribution of gas molecules in the atmosphere of the earth. The potential energy of a gas molecule with mass ' $m$ ' (relative to its value at the surface of the earth) equals  $mg\Delta h$ , where  $\Delta h$  is the difference in height above the surface of the earth:

$$\ln \frac{c}{c^o} = \frac{-mg\Delta h}{kT} \quad (2.1.4)$$

Thus, when the temperature is constant and independent of the height, the concentration gas molecules will decrease logarithmically with the height. For ions in an electrolyte solution it applies that at a certain point in the solution an electric potential exists. The concentration positive ions in that zone equals equation 2.1.5. The concentration negative ions equals to equation 2.1.6. This potential becomes the same as the gravitational field of the earth and arises from the charge of the ion. The charge of the ion gives an opposite 'charge' around the ion.

$$c(+)=c^o \exp(-z_+e\Phi/kT) \quad (2.1.5)$$

$$c(-)=c^o \exp(+z_-e\Phi/kT) \quad (2.1.6)$$

$e$  = Elementary proton charge.

$z$  = Positive or negative valence of the ion.

$\Phi$  = Electrical potential.

$c^o$  = Concentration positive/negative ions at point  $\Phi = 0$ .

The value for  $\Phi$ , near to a negative charged ion, will be negative. Therefore, the sum of  $[c(+)-c(-)]$  will be positive:

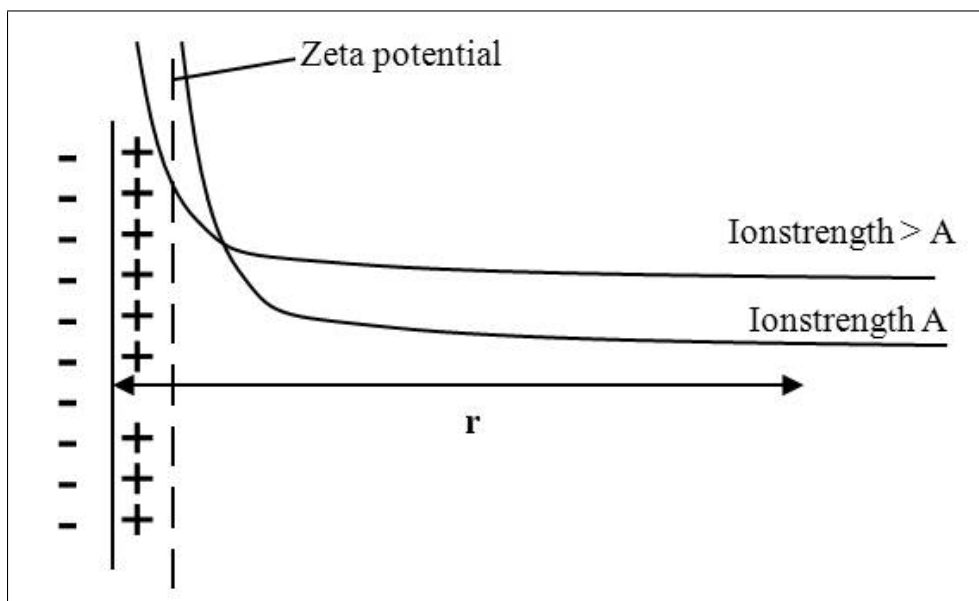
$$[c(+)-c(-)] = c^o \exp(-z_+e\Phi/kT) - c^o \exp(+z_-e\Phi/kT) \quad (2.1.7)$$

**For example:**  $\Phi = -1$ , the equation becomes:  $[c(+)-c(-)] = c^o \exp(z_+e/kT) + c^o \exp(z_-e/kT)$

The charge around a negative ion is positive and is also known as the electron cloud (for a positive ion it is the other way around). In the colloid science, people are mainly interested in the electron cloud around a charged colloidal particle instead of that of one ion. Instead of a electron cloud it is also called an electric double layer. The charge on a particle is distributed over the surface and is balanced with the opposite charge in the electric double layer where an excess of counter-ions is present. The potential on the surface is called zeta potential and is often expressed in millivolt.

Imagine that two particles with the same zeta potential moves individually from each other in a solution. When there is a significant overlap of the double layer, one particle can interact with the other (increase of electrostatic repulsion). The particles will repel each other when the particles come too close to each other. When an electrolyte solution is added (increasing the ion concentration) the thickness of the double layer decreases (Figure 2.2). This decrease means that the particles can be closer to each other than before. Therefore, it is not strange that this could be an unstable situation for colloidal particles. However, for raspberry-like particles this information is useful. This project is all about small spherical particles adsorbed on to the surface of larger spherical particles (raspberry-like particles). When the small particles are on the surface of the larger particles, the behavior of the small particles will be the same as the larger particles: when the particles come too close to each other, it will result in repulsion. The coverage of the large particles has to be high for making the raspberry-like particles as rough as possible. This can simply be done by raising the ion concentration. However, when the concentration is too high it can lead to two situations: Coagulation through instability (concerning the total system) or a decrease in roughness through too much covering.

As mentioned above, the strength that one particle can interact with the other particle depends on the distance between the particle. To speak in the correct term for this phenomenon, the term Debye-length<sup>[6],[7]</sup> is used. A short Debye-length means that the particles can be close to each other before they interact (the strength of interaction is strong). A long Debye-length means that the particles interact at a greater distance (the strength of interaction is less strong). The Debye-length is given as  $\kappa^{-1}$  and defined as:



**Figure 2.2:** This figure shows schematically that two particles can be closer together when the ion concentration increases.

$$\kappa^{-1} = \sqrt{\frac{\varepsilon_r \varepsilon_0 k_B T}{x N_A e^2 I}} \quad (2.1.8)$$

$\varepsilon_r$  Dielectric constant of the medium.

$\varepsilon_0$  = Dielectric constant of free space.

$k_B$  = Boltzmann constant.

$T$  = Temperature (K).

$x$  = The number of atoms from the electrolyte. Example:  $\text{NaCl (s)} + \text{H}_2\text{O} \longrightarrow \text{Na}^+ + \text{Cl}^-$  ( $x=2$ ).

$N_A$  = Avogadro number.

$e^2$  = Elementary charge.

$I$  = Ionic strength of the electrolyte ( $\text{mol/m}^3$ ).

There are a lot of constants that can be combined to one constant value. Leaving the variables  $\varepsilon_r$ , temperature,  $x$  and the ionic strength of the electrolyte. It often happens that water is the medium and the temperature is 298 Kelvin. Furthermore, common electrolytes have the ratio 1:1. For example:

- Sodium chloride ( $\text{Na}_1\text{Cl}_1$ ).
- Potassium chloride ( $\text{K}_1\text{Cl}_1$ ).

Therefore, the formula for the Debye length (for 1:1 electrolyte aqueous solution at room temperature) simplifies to:

$$\kappa^{-1} = \frac{0.304}{\sqrt{I(M)}} \quad (2.1.9)$$

Where " $I$ " stands for the ionic strength of the electrolyte solution in  $\text{mol}\cdot\text{L}^{-1}$ . Therefore, an increase in salt concentration results in a shorter Debye-length. The small particles on the surface of the large particles can be closer together, so a higher coverage is reached.

### Steric repulsion

Steric repulsion is another way to stabilize dispersions. This can be done with components that have a low solubility in the polymerization medium and with an average affinity to the polymer particles, like synthetic polymers. One part of the polymers is attracted by the particles and the other part is more attracted to the solvent. Therefore, the particle can be hydrophobic and the solvent hydrophilic (or the other way around). The hydrophobic part of the polymer will be on the particle and the hydrophilic part in the solvent. The polymer chains of multiple particles will hinder each other sterically, which leads to repulsion. This kind of systems is also called polymer brushes.

### 2.1.2 Synthesis

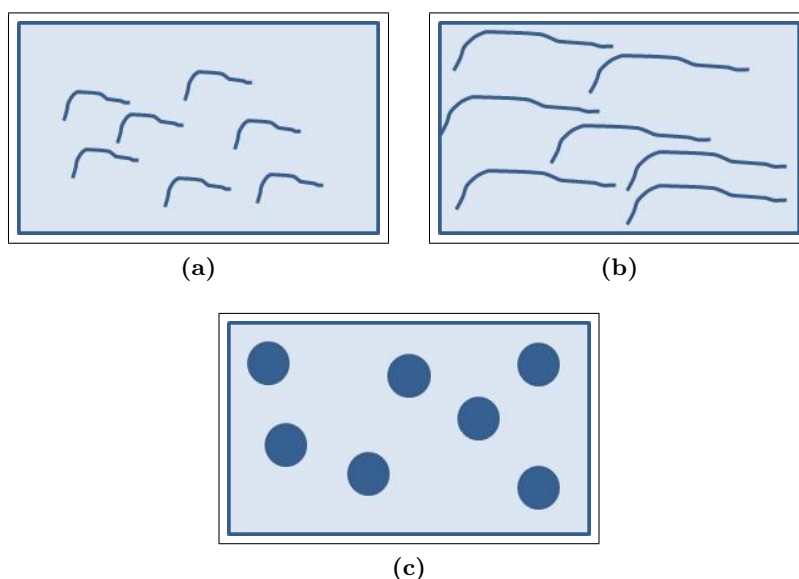
Since dispersions can be stable it is useful to know how dispersion can be made. This can be done with dispersion methods and with condensation (or nucleation) methods. With dispersion methods it is all about breaking down bulk matter to colloidal dimensions. With nucleation methods it is all about building up molecular aggregates to colloidal sizes. This thesis will be limited to the nucleation methods.

With nucleation methods, molecular complexes need to be formed of increasing size until the colloid size range is reached. Usually the molecular or atomic species are formed by a chemical reaction and are virtually insoluble in the dispersion medium. Therefore, the species will aggregate into particles of increasing size. The conditions have to be carefully chosen or else the

meta-stable equilibrium will not exist (then the dispersion is not stable) and coagulation takes place. The conditions which are important:

- The stock of molecules or atoms needs to react as soon as possible when the particles have a colloidal size. This means that the solutions are very diluted.
- As much as possible nuclei have to be formed in a short as possible time.
- There have to be an appropriate stabilization mechanism operative. This could be opposite charges, (double) electrolyte layer or steric stabilization.

Nucleation is the development of a new phase in an already existing phase. When a lot of the nuclei are formed in a really short time, nucleation will stop. The nuclei that are already formed will grow (with the same speed) to form particles. Theoretically this can be obtained when the reactants (the precipitating particles) take a concentration level just above the critical super saturation point. This means that there are more reactants dissolved in the solvent than the solvent can handle (under normal circumstances). This results in a spontaneous nucleation that reduces the concentration to just below the critical super saturation point. The growth process is now the favorite process instead of the production of new nuclei. The time that the nuclei are formed is important because this time determines the size distributions of the particles. The shorter the time the narrower the size distribution is. Therefore, it is possible to form monodisperse particles with tunable colloid size<sup>[6]</sup>. Figure 2.3a, 2.3b and 2.3c shows schematically the nucleation process. The particles have a spherical shape because after nucleation the particles are not soluble anymore. The size of the spherical particles in figure 2.3c can still grow or "swell" further.



**Figure 2.3:** Figure (a) shows that nuclei are formed and chains already started to grow. This phase is soluble in the polymerization medium. Figure (b) shows that the chains are growing and that the chains are still soluble in the polymerization medium. Figure (c) shows that the molecular weight reach some point that the chains are not soluble anymore in the polymerization medium and nucleation took place.

There are several methods to synthesize colloidal dispersions. Arshady listed a few types of polymerization techniques in an article<sup>[8]</sup> and these are the most important types for this thesis:

- **Classic Emulsion Polymerization**

The surfactant forms micelles in the medium, the initiator is medium soluble, the monomer and polymer are not medium soluble. The reaction goes as follows: The initiator decomposes in radicals when the temperature is high enough. Therefore, monomer-radicals will be formed when the radicals meet monomers. The monomer-radicals will polymerize in the micelles. The growth process will stop when there are no monomers left or when an agent is added that extinguishes the radicals.

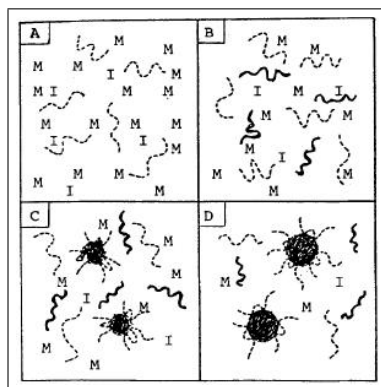
- **Surfactant-free Emulsion Polymerization**

The initiator is medium soluble, the monomer and polymer are not medium soluble. The reaction goes as follows: The radicals are formed in the medium through heating and the radicals will meet monomers. These relatively short chains will polymerize by reacting with monomers. At some moment nucleation will take place by precipitation of macroradicals. As long as the process polymerizes the particles are getting bigger. The particles will not be stable because of the absence of surfactant. However, there will be a form of stabilization because of the end groups of the chains. Polymer chains end with a radical (for example potassium persulphate) and therefore it looks like this:  $\sim\text{polymer chain-O-SO}_3^-\text{K}^+$ . These electrostatic charges will stabilize the chains through repulsion. To make such systems possible, the concentration of monomers has to be very low or else coagulation will take the overhand. The particles that are formed vary in size from 100 to 1000 nanometer. The particle size can be tuned by tuning the ratio of monomer and initiator.

- **Dispersion Polymerization**

The monomers and initiator are both soluble in the polymerization medium, but the medium is not a good solvent for the resulting polymer. The reaction goes as follows (Figure 2.4): Through heating the initiator decomposes in radicals and monomer-radicals are formed when these radicals meet the monomers. The polymerization also takes place in the same medium. When the polymer is not soluble anymore in the medium (relatively quickly, depending on the solvent) nucleation takes place. The primary particles that are formed can swell further through the monomers. This results in spherical particles from 100 to 1000 nanometer. The difference in the size depends on the initiator concentration, monomer concentration, temperature and the solubility.

Colloidal dispersion that are formed by dispersion polymerization are not stable without stabilizer. Therefore, coagulation takes place during the formation. A small percentage of an appropriate stabilizer is already enough to stabilize the dispersion.



**Figure 2.4:** This figure shows schematically the growth process of dispersion polymerization. M = Monomer and I = initiator<sup>[8]</sup>.

## 2.2 Syntheses from Literature

Now there is more known about colloids and different polymerization techniques with corresponding terms, the work of other people can be studied. Nanidiyanto<sup>[5]</sup> and Goodwin<sup>[9]</sup> have been working on surfactant-free emulsion polymerization of positively charged polystyrene. The polymerizations were carried out several times under different temperatures, monomer and initiator concentrations. This was done to see if there are any influences on the particle size. Summarized (see Fig 2.5):

- **Temperature**

Increasing the temperature ( $T_{\text{minimum}}$  = decompose temperature of the initiator) with several initiator and monomer concentrations results in a decrease of the particle size.

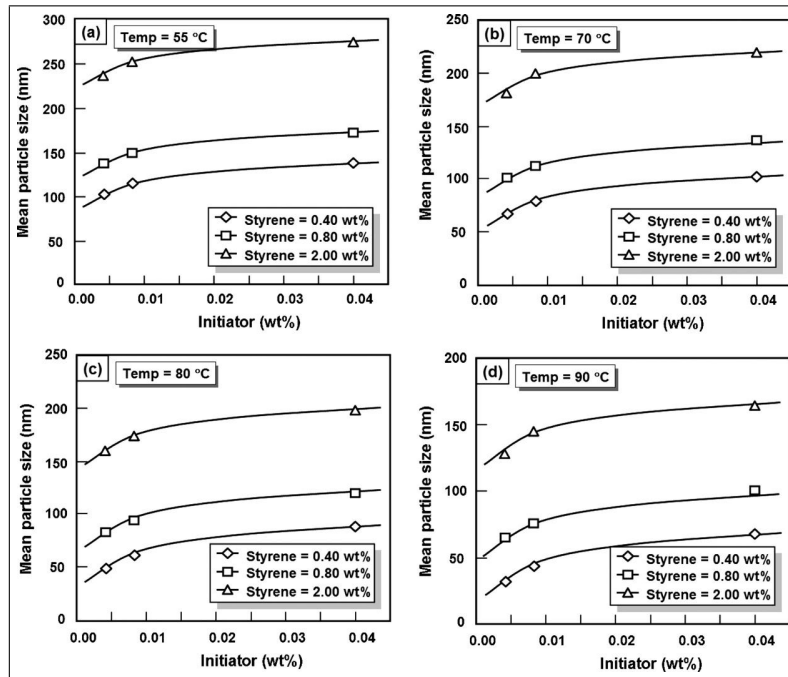
- **Initiator Concentration**

Increasing the initiator concentration with several temperatures and monomer concentrations results in a small increase of the particle size. There is a maximum at 0.04% wt (weight) when AIBA (2,2-azobis(2-methylpropionamide) dihydrochloride) as initiator is used. The amount of initiator is direct related with the amount of seed particles. The same amount of monomers have to be shared with more seed particles when the initiator concentration is higher. This is why the initiator concentration has a relative small influence on the particle size.

- **Monomer Concentration**

Increasing the monomer concentration with several temperatures and initiator concentrations results in a larger increase of the particle size up to a certain limit. This has a larger influence than the initiator concentration because the seed particles can grow larger when there are more monomers. When the styrene concentration is too high, the particles can not repel each other anymore and start to aggregate.

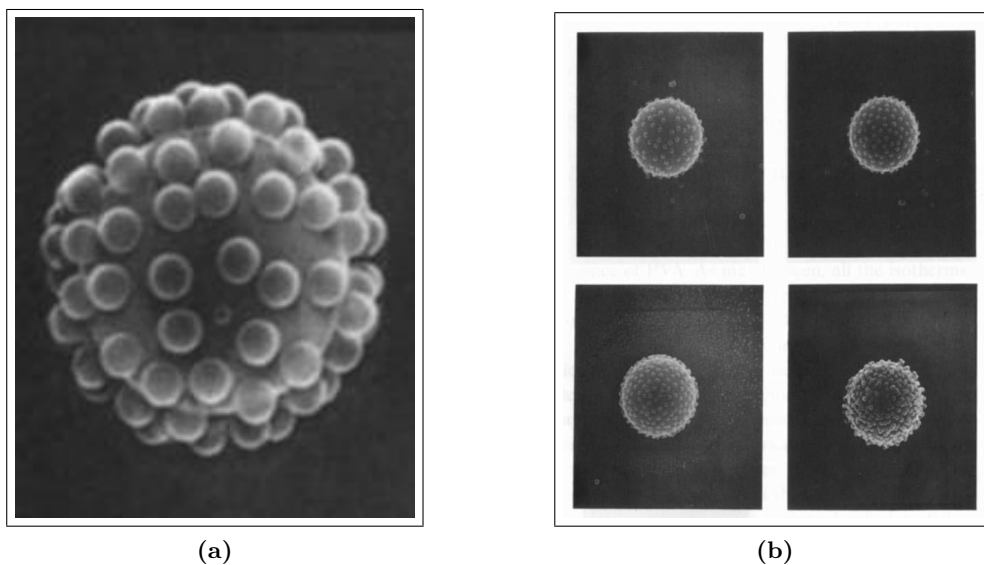
Therefore, in this synthesize the particle size can be varied with temperature, initiator concentration and styrene concentration.



**Figure 2.5:** This figure shows how the particle size changes with different monomer, initiator concentrations and temperatures<sup>[5]</sup>.

Harley<sup>[1]</sup> used positively charged polystyrene particles as seed particles for the synthesis of raspberry like particles. The small particles were negatively charged polystyrene particles. An electrolyte solution is added to the small and large particles to influence the coverage. The amount of covering was studied when the electrolyte concentration changes. Figure 2.6a shows the result for so far. Figure 2.6b shows that the electrolyte concentration influence the surface coverage of the positive particles. When the electrolyte concentration is zero there will be a relatively low coverage. When the electrolyte concentration increases, the coverage will increase. There is a point where the coverage is maximum and this point is called the critical electrolyte concentration (CEC). If the CEC is reached it means that the small negative particles are starting to form clusters on the surface of the positive large particles. Therefore, the electrolyte concentration can influence the coverage of the raspberry like particles until some maximum:  $electrolyteconcentration < CEC$ .

A thin-film freeze-drying scanning electron microscope (TFFDSEM) was used to check if raspberry-like particles were formed. As the name says, a thin film (sample) is freeze dried and after that it is analyzed with a scanning electron microscope. In practice this is a bit complicated because the freezing has to go fast enough to avoid ice crystal formation. If this is successful, the method give some excellent results for the study to small particles adsorbed onto larger particles. TFFD-SEM has proofed that the electrolyte concentration is an important parameter for the covering of the particle.



**Figure 2.6:** Figure (a) shows an electron microscope view of small negative polystyrene particles absorbed on the surface of the bigger positive charged particles<sup>[1]</sup>. Figure (b) shows an increase in electrolyte concentration from left above to right below<sup>[1]</sup>.

## 2.3 Calculation for the Coverage

Balmer<sup>[10]</sup> did some calculation work on the coverage of small silica particles onto large sterically stabilized poly(2-vinylpyridine) latex particles in aqueous solution. This is another system than the system in this project but it is a method to determine a value for the coverage of the surface. The formula in Equation 2.3.1 is the outcome and Figure 2.7 gives a better view of the situation.

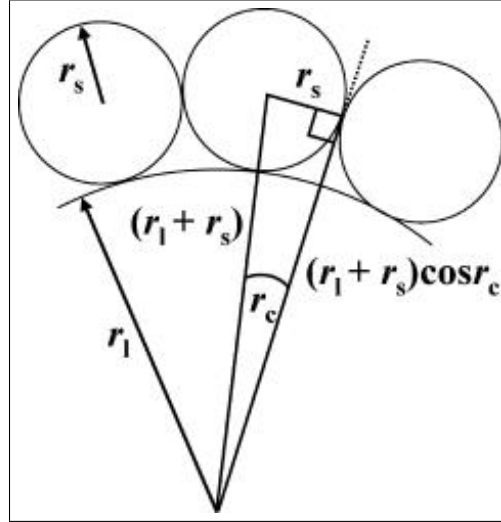
$$P \cong \frac{Nr_s^2}{4(r_1 + r_s)^2} \quad (2.3.1)$$

$P$  = Coverage

$N$  = The amount of small particles onto the surface of one large particle

$r_s$  = The radius of a small particle

$r_l$  = The radius of a large particle



**Figure 2.7:** Schematically representation of the geometric considerations for the packing of small spheres, of radius  $r_s$ , around a large sphere, of radius  $r_l$ . The raspberry-like particles defines a sphere of radius  $(r_l + r_s)$ <sup>[10]</sup>.

Equation 2.3.1 relates " $P$ " with " $N$ " but there is still more information needed to determine one of the two. Computer simulations were done to calculate the theoretical coverage<sup>[11]</sup>. The "real" coverage differs from the theoretical because it is another system than that of Balmer. Furthermore, certain salt concentrations are going to be used and this influence the coverage. This is why the computer calculations will not be used. Therefore, the calculation below is an approximation for the coverage based on a chosen coverage and on Equation 2.3.1.

The radius of the small and large particles have to be known (Zetasizer or TEM) to determine  $N$  since the coverage can be set on every number that the analyst wants. When this is achieved, the ratio between small and large particles is known:  $N : 1$ . Further information that needs to be known:

- Theoretical coverage  $P$  or a chosen coverage: 0.8.
- Solid content of the large polystyrene particles and the solid content of the small polystyrene particles:  $SC_l$  and  $SC_s$  respectively.
- Formula for the volume of a sphere:  $V = 4/3\pi r^3$  ( $r$  = radius (m)). This can be done for the small and large particles.
- Density of polystyrene:  $\rho_{\text{polystyrene}} = 1060 \text{ kg/m}^3$ .

The weight ratio of small:large spheres is:  $N \cdot V_s \cdot \rho_{\text{ps}} = X_s \text{ (kg)}$  and  $1 \cdot V_l \cdot \rho_{\text{ps}} = X_l \text{ (kg)}$  results in  $X_s : X_l$ . Since the SC of the dispersions small and large particles is known, the amounts of dispersions can be easily calculated. Therefore, a simple and logic conclusion is that the dispersion amounts determines the covering of the raspberry-like particles (when the radius is fixed!).

## 2.4 Analysis Methods

This section contains some information about the operation of the Zetasizer and the TEM to understand the obtained values for the particle sizes. It will be two brief descriptions, because the measuring equipment are very detailed processes and this is not the focus of the project.

### 2.4.1 Zetasizer

The measurements of interest from the zetasizer concerning this project are the size and the zeta potential.

#### Size

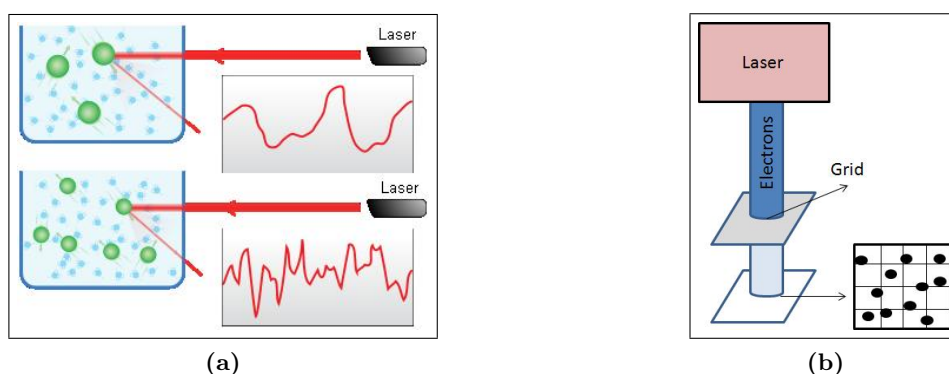
Particles in suspension undergo random Brownian motion. If these particles are illuminated with a laser beam, the intensity of the scattered light fluctuates at a rate that is dependent upon the size of the particles (figure 2.8a). The technique of Dynamic Light Scattering (DLS) analyses these intensity fluctuations to determine the velocity of the Brownian motion and hence the particle size. Small and large particles do not scatter the light the same way and therefore the scattering can be measured at two angles. The measurement can be set on forward scattering ( $13^\circ$ ), back scattering ( $173^\circ$ ) or dual angle. Large particle scatter the light especially forward and small particles scatter the light everywhere. The measurement can be set on dual angle, when there is a doubt if the particle belongs to the small or to the large group. It can also be used to see which results are more constant and/or reliable.

#### Zeta potential

The zeta potential is the overall charge a particle acquires in a particular medium and is a measure of the electrostatic interaction between particles. In general, the higher the zeta potential of a sample, the more likely the dispersion will remain stable. Laser Doppler electrophoresis is a technique used to measure the movement of charged particles in an electric field which utilizes the well-known Doppler effect. Light scattered from a moving particle experiences a frequency shift. This frequency shift can be determined using phase analysis light scattering (PASL). The magnitude of the frequency shift is determined by the zeta potential of the particles.

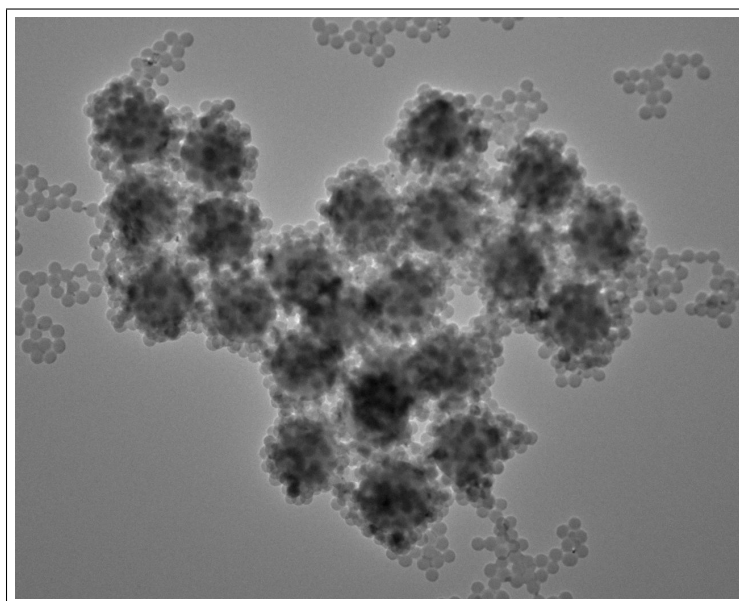
### 2.4.2 TEM

Transmission Electron Microscope transmits electrons through a small substrate (sort of counting chamber). This substrate contains the dried sample of interest. The transmitted electrons

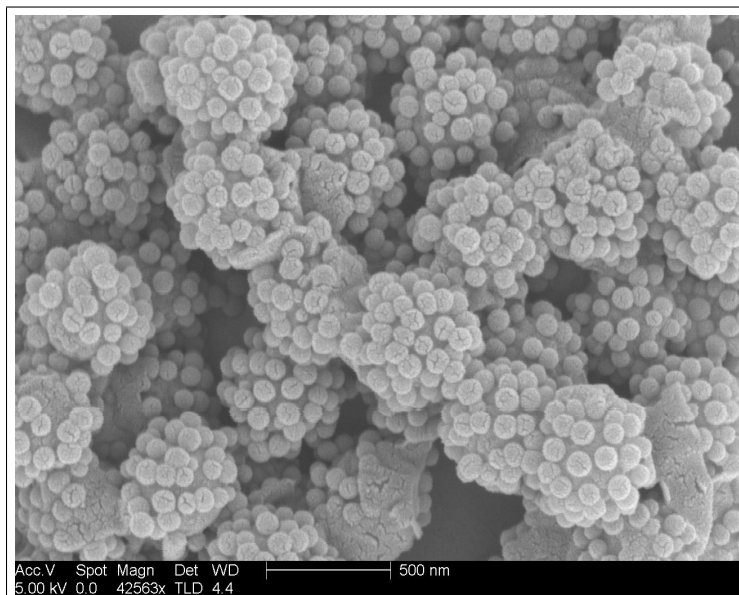


**Figure 2.8:** Fig (a) shows that the scattered light fluctuates at a rate that is dependent upon the size of the particles<sup>[12]</sup>. Fig (b) shows schematic how a TEM works. The result can be seen as an image from the shadows of the particles.

will go through the substrate and the particles absorb the electrons. This results in an intensity difference, which are spots with the shape of the particles and the "chambers". This is made evident by an electron sensitive plate/camera (fig 2.8b). Therefore, the analyst can see the "chambers" where the particles are in with associated shapes (at nanometer resolution). Images can be saved when a camera is used. The particle size can be determined from these images (using the corresponding software program). Scanning Electron Microscope (SEM) is almost the same but with this technique it is not about the transmitted electrons that are creating an image of the particles, but about the scattered electrons that create an image of the particle surface. TEM gives a 2D view (Fig 2.9a) and SEM a "3D" view (Fig 2.9b).



(a)



(b)

**Figure 2.9:** Fig (a) shows an image of raspberry-like particles that is made with a TEM. Fig (b) shows an image of raspberry-like particles that is made with a SEM.

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# Experimental

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The experimental chapter will be divided in three sections:

- Synthesis of Positively Charged Polystyrene Particles
- Synthesis of Negatively Charged Polystyrene Particles
- Forming of Raspberry-like Particles

### 3.1 Synthesis of Positively Charged Polystyrene Particles

#### Method A

Positively charged polystyrene particles were synthesized using the method from Nandiyanto<sup>[5]</sup>. A 200 ml round bottom flask equipped with a mechanical stirrer mechanism contained 1 ml 40.32 g·L<sup>-1</sup> AIBA (Acros 99% purity, 0.040% wt) and 98 g water. The environment was made oxygen free through flushing it with nitrogen gas (while stirring). The round bottom flask was heated up to 55°C utilizing an oil bath. 2.2 mL distilled styrene (Sigma-Aldrich ≥ 99% purity, 2.0% wt) was added after that the temperature reached 55°C. The synthesis was carried out further at 55°C for 24 hours while stirring. Distilled styrene was used to remove inhibitors.

Purification was done by centrifugation at 3750 round per minute for five hours. After centrifugation, the sediment was redispersed in water.

#### Method B

Positively charged polystyrene particles were synthesized using the method from Duracher<sup>[13]</sup>. A 100 mL round bottom flask equipped with a stirring bar contained 50 g water, 50.0 mg AIBA (0.091%wt), 5.00 mL styrene (8.2% wt) and 0.505 g N-isopropylacrylamide (NIPAM, Aldrich 97% purity, 0.92% wt). The round bottom flask was made oxygen free by flushing it with nitrogen gas for 20 minutes (while stirring). After that, the round bottom flask was put 10 minutes in an ultrasonic-bath for better mixing. Finally, the round bottom flask was immersed in an oil bath of 70°C and stirred for 24 hours.

After 24 hours mixing, a shot of 6.25 g water, 31.6 mg AIBA (0.415% wt), 1.27 g NIPAM (16.7% wt), 38.3 mg 2-aminoethylmethacrylate hydrochloride (AEM, Acros 99% purity, 0.503% wt) and 18.6 mg methylenabisacrylamide (MBA, Sigma ≥ 98% purity, 0.244% wt) was added to make the seed particles larger. After the shot was added, the mixture was stirred for another 24 hours at 70°C.

Purification was done by centrifugation at 3750 round per minute for three hours. After centrifugation, the sediment was redispersed in water.

### Method A & B

The characterization of the positive particles was mainly done with two types of instruments:

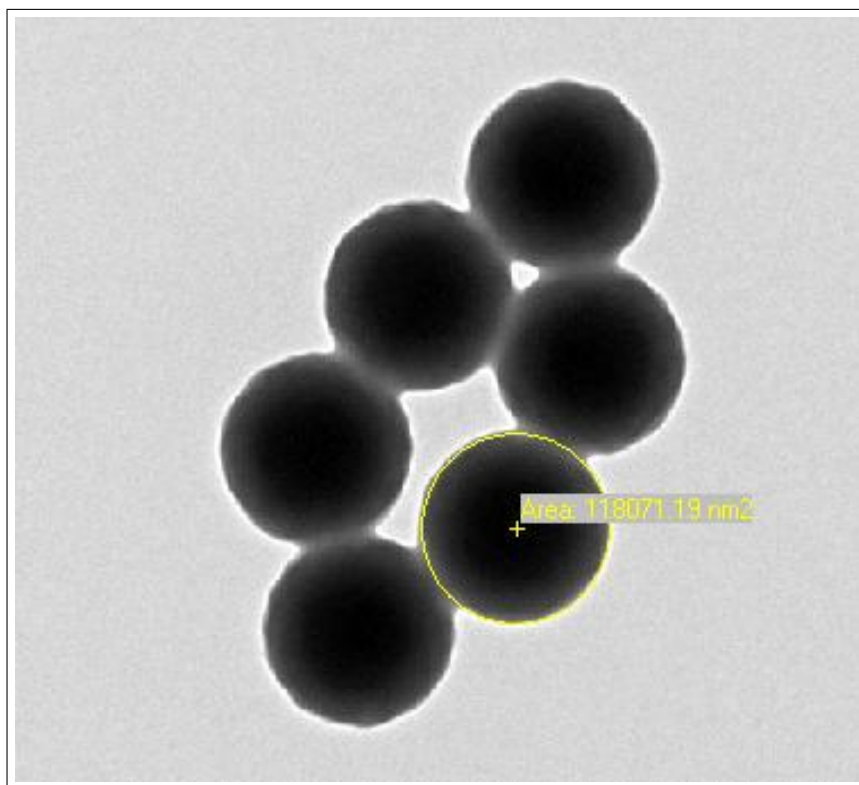
- Zetasizer (Malvern Zetasizer Nano-series ZEN 3600)

**Settings for the size:** *Material:* Polystyrene latex, *Dispersant:* Water, *Temperature:* 25°C, *Equalibration time:* 120 seconds, *Cell:* DTS0012-Disposable sizing cuvette, *Measurement:* Dual angle, 8 measurements, 0 seconds delay between measurements.

**Settings for the zeta potential:** *Material:* Polystyrene latex, *Dispersant:* Water, *General options:* Fka selection model smoluchowski, 1.50 F(Ka), *Temperature:* 25°C, *Equalibration time:* 120 seconds, *Cell:* DTS1060C-Clear disposable zeta cell, *Measurement:* Duration minimal 52 and maximal 100 runs, 8 measurements.

**Temperature test VS Size:** A temperature test was preformed to see if the particle size changes with changing temperature. This was done with the zetasizer and the settings were the same as above. Only the temperature was changed and the file was saved again. Then all the files with the adjusted temperatures were put in a "play list" and the measurement was started.

- TEM (Philips TECNAI 10): A droplet of diluted sample was put on a substrate. This substrate was dried under a halogen lamp and imaged using TEM. The particle size can be determined from the saved images using iTEM, a software program. Three points have to be putted on the edge of a spherical particle (distributed) and iTEM draws a circle (Fig 3.1).



**Figure 3.1:** TEM image of spherical particles. The area can be determined by drawing a circle with iTEM. When this is done, the radius is also determined: 193.86 d.nm (from the particle with a yellow circle).

Other characterizations like the solid content and the conversion of the reaction were determined manually. A known amount of sample was dried under a halogen lamp and after that it was weighed again. From these weights the solid content and conversion were calculated (Equation 3.1.1 and Equation 3.1.2 respectively).

$$SolidContent(\%) = \frac{SampleDried}{SampleWet} * 100\% \quad (3.1.1)$$

$$Conversion(\%) = \frac{SolidContent(g)}{Monomers(g)} * 100\% \quad (3.1.2)$$

## 3.2 Synthesis of Negatively Charged Polystyrene Particles

These particles were provided by Bas van Ravensteijn and were synthesized with the following method. Cross-linked polystyrene (CPs) particles were synthesized using a standard emulsion polymerization described in literature. A 500 mL round bottom flask equipped with stir bar was placed in an oil bath of 80°C. 200 mL Milli-Q water was charged into the reactor and allowed to reach the bath temperature. 21.15 g styrene (6.80%wt), 0.635 g DVB (divinyl benzene, 0.204%wt) and 0.25 g of SDS (sodium dodecyl sulfate, 0.0804%wt) dissolved in 50 mL Milli-Q water were added. The complete mixture was allowed to heat up to the temperature of the bath. Finally, addition of 1.55 gram of KPS (potassium persulfate, 0.498%wt) dissolved in 37.5 mL Milli-Q water initiated the polymerization. Reaction was allowed to continue for 24 hours at 80°C.

The characterizations were done with the same measurements and settings as the positive polystyrene particles.

## 3.3 Forming of Raspberry-like Particles

For 1% solid content raspberry-like particles and a coverage of 80%<sup>[10]</sup>, the following quantities were mixed in this sequence: 0.400 ml 0.1 M NaCl, 1.890 ml water, 1.096 mL PS+ (positive polystyrene particles, 27.40% wt) and 0.614 ml PS- (negative polystyrene particles, 15.35% wt) resulted in a total volume of 4.000 mL.

The characterizations of the raspberry-like particles were done with:

- Zetasizer (Malvern Zetasizer Nano-series ZEN 3600). The settings for the dispersant were varied from 0.1M NaCl to 0.001M NaCl. It depends on the salt concentration of the sample.
- TEM (Philips TECNAI 10)
- SEM (Philips XL 30-series): Same preparations as the TEM but before measuring, the substrate was sputter coated with a 6 nm platinum layer(for conducting the electrons).



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## Results and Discussion

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This chapter gives the results and discusses the results from the experimental section. Therefore, this chapter is also divided in three sections:

- Results of Positively Charged Polystyrene Particles
- Results of Negatively Charged Polystyrene Particles
- Results of Raspberry-like Particles

### 4.1 Results of Positively Charged Polystyrene Particles

The goal was to obtain stable positive polystyrene particles of  $\sim 300$  nm in diameter (d.nm). The first badge that was synthesized (PS+01) was based on the synthesis in an article of Nandiyanto<sup>[5]</sup>. The badges after PS+01 until PS+05 were adjusted to make the particles larger, make the dispersion less aggregated, increase the conversion and/or make the particles more mono-disperse. Table 4.1 shows the synthesis conditions that were changed for the adjustments and Table 4.2 and 4.3 shows the synthesis results that were measured.

**Table 4.1:** The synthesis conditions of the different positive polystyrene particles that were synthesized with method A.

| Sample | Styrene (mL) | AIBA (mg) | Milli-Q (g) | Temperature (°C) | Reaction time (hours) |
|--------|--------------|-----------|-------------|------------------|-----------------------|
| PS+01  | 2.20         | 40.3      | 98.3        | 55               | 21                    |
| PS+02  | 3.30         | 21.0      | 97.2        | 55               | 23                    |
| PS+03  | 5.00         | 6.97      | 50.4        | 70               | 21                    |
| PS+04  | 5.00         | 6.89      | 50.0        | 70               | 24                    |
| PS+05  | 5.00         | 7.18      | 49.9        | 60               | 24                    |

Sample **PS+01** was carried out according to method A from the experimental section (Section 3.1, method A). The round bottom flask contained a little bit of white solid at the wall, indicating that some aggregation had taken place during the synthesis. The results in Table 4.2 shows that the size of the particles were not big enough (224.1 d.nm) and also that the solid content and the conversion are relatively low (respectively 0.36% and 18%). It could be that the amount of initiator was too high (too many nuclei were formed) and the amount of monomers is too low (not enough monomers to grow to a larger size). Therefore, the next synthesis (PS+02) contained less initiator and more styrene.

**Table 4.2:** Synthesis results of the positive polystyrene particles, method A.

| Sample             | TEM size (d.nm)   | Solid content (%) | Conversion (%) | Aggregation? |
|--------------------|-------------------|-------------------|----------------|--------------|
| PS+01              | 224.1 $\pm$ 14.6% | 0.36              | 18             | A little bit |
| PS+02              | 106.3 $\pm$ 22.8% | 0.036             | 1.2            | A little bit |
| PS+03 <sup>1</sup> | 363.7 $\pm$ 11.0% | 4.4               | 54             | A lot of     |
| PS+04 <sup>1</sup> | 309.4 $\pm$ 2.64% | 3.9               | 47             | A little bit |
| PS+05 <sup>1</sup> | 233.8 $\pm$ 8.50% | 0.63              | 7.6            | A little bit |

**Table 4.3:** Zetasizer measurements of the positive polystyrene particles, method A.

| Sample             | Zetasize backscattering (d.nm) | Zetasize forward scattering (d.nm) | Zetapotential (mV) |
|--------------------|--------------------------------|------------------------------------|--------------------|
| PS+01              | 194.7                          | 252.8                              | 33.80              |
| PS+02              | 139.2                          | 170.5                              | 28.28              |
| PS+03 <sup>1</sup> | 405.1                          | 385.9                              | 0.8460             |
| PS+04 <sup>1</sup> | 335.0                          | 299.3                              | 16.39              |
| PS+05 <sup>1</sup> | 251.9                          | 407.1                              | 36.81              |

During the synthesis of **PS+02** there was also some aggregation formed (little bit white solid at the wall of the round bottom flask). Furthermore, PS+02 smelled like styrene which gave the idea that a part of the styrene had not reacted. The results in Table 4.2 confirmed this because the particle size is relatively small (106.3 d.nm, not much progress in the growth) and the solid content and the conversion were very low (respectively 0.036% and 1.2%). A reason could be that a part of the added initiator was not decomposed, because 55°C is the decomposition temperature of AIBA. Therefore, the next synthesis (PS+03) was carried out at 70°C. PS+03 will also contain even less initiator and more styrene than PS+02. Furthermore, the round bottom flask will be held in an ultrasonic bath for three minutes (for better mixing of the styrene, AIBA and water phase) before the reaction starts.

During the synthesis of **PS+03** it looked like that the stirring was not optimal. After the synthesis there was a lot of aggregation formed. Table 4.2 shows that not only the particles size is improved (363.7 d.nm) but also the solid content and the conversion were improved (respectively 4.4% and 54%). However, Table 4.3 shows that the zeta potential is relatively low (0.8460 millivolt (mV)). This probably also caused the large amount of aggregation. The particles had not enough charge on the surface, therefore aggregation took place and this resulted in a lot of white solid in the flask. The amount of aggregation could also have been due to the fact that the mixing during the synthesis was not optimal. Therefore, PS+04 will contain the same quantities but with a stirring bar instead of a mechanical stirrer and the ultrasonication time will be extended to five minutes (maybe three minutes was too short).

After the synthesis of **PS+04**, the round bottom flask contained a little bit of white solid at the wall, indicating that some aggregation had taken place during the synthesis. The zeta potential had improved a lot (16.39 mV), but it is still a bit low. The particle size decreased, but it is still large enough (309.4 d.nm). Furthermore, also the solid content and the conversion decreased a little bit (respectively 3.9% and 47%). The next synthesis will have a longer extended ultrasonication time, because the first extension improved the zeta potential significantly.

**PS+05** had less white solid at the wall of the round bottom flask than PS+04, which indicates that there is less aggregation formed. The zeta potential was again improved (36.81 mV). How-

<sup>1</sup>The measurements of the sample were done after five hours of centrifugation at 3750 rpm (rounds per minute).

ever the particle size decreased a lot (233.8 d.nm), just like the solid content and the conversion (respectively (0.63% and 7.6%). It seems that this method does not work to obtain the desired particle size  $\sim 300$  d.nm with a zeta potential of 20 – 30 mV. Therefore, another idea has to be developed.

The next synthesis was carried out according to method B from the experimental section (Section 3.1, method B). First there will be seeds co-polymerized using the monomers styrene and NIPAM. NIPAM has been chosen, because it is known that pNIPAM adsorbs readily on polystyrene. The second step is to co-polymerize the seed particles further, so a larger particle size can be achieved. The synthesis conditions can be found in Table 4.4

**Table 4.4:** Synthesis conditions of the positive polystyrene particles, method B

| Sample              | Styrene (mL) | AIBA (mg) | NIPAM (g) | Milli-Q (g) | AEM (mg) | MBA (mg) |
|---------------------|--------------|-----------|-----------|-------------|----------|----------|
| PS+07 <b>Step 1</b> | 5.00         | 50.8      | 0.505     | 50.0        | 0.00     | 0.00     |
| PS+07 <b>Step 2</b> | 0.00         | 31.6      | 1.27      | 6.27        | 38.3     | 18.6     |
| PS+08               | 5.00         | 50.4      | 0.507     | 50.0        | 0.00     | 0.00     |

When part one of **PS+07** was finished, there was observed a little bit white solid at the wall of the round bottom flask. A sample was taken and measured on zeta potential (36.8 mV), particle size (385.3 d.nm), solid content (8.06%) and conversion (88.7%). The values can be found in Table 4.5 and 4.6). These results are very good because the particle size corresponds to the goal, the zetapotential is enough to prevent aggregation and the conversion is relatively high. Step two was still preformed to see the effect of it. The second step was added as a shot. This was not easy to dissolve, because there were a lot of solids in a small amount of water. Therefore, a relatively large amount of solid was left in the preprocessing tube. The round-bottom flask contained a lot of aggregation after the reaction. The results of the TEM (a lot of clusters) and Zetasizer (large particle sizes) confirmed the idea that there was a lot of aggregation. Step two has no positive influence on the particles. The next synthesis (PS+08) will be a copy of PS+07 (the first step) to see if the same results can be achieved.

**Table 4.5:** Synthesis results of the positive polystyrene particles, method B

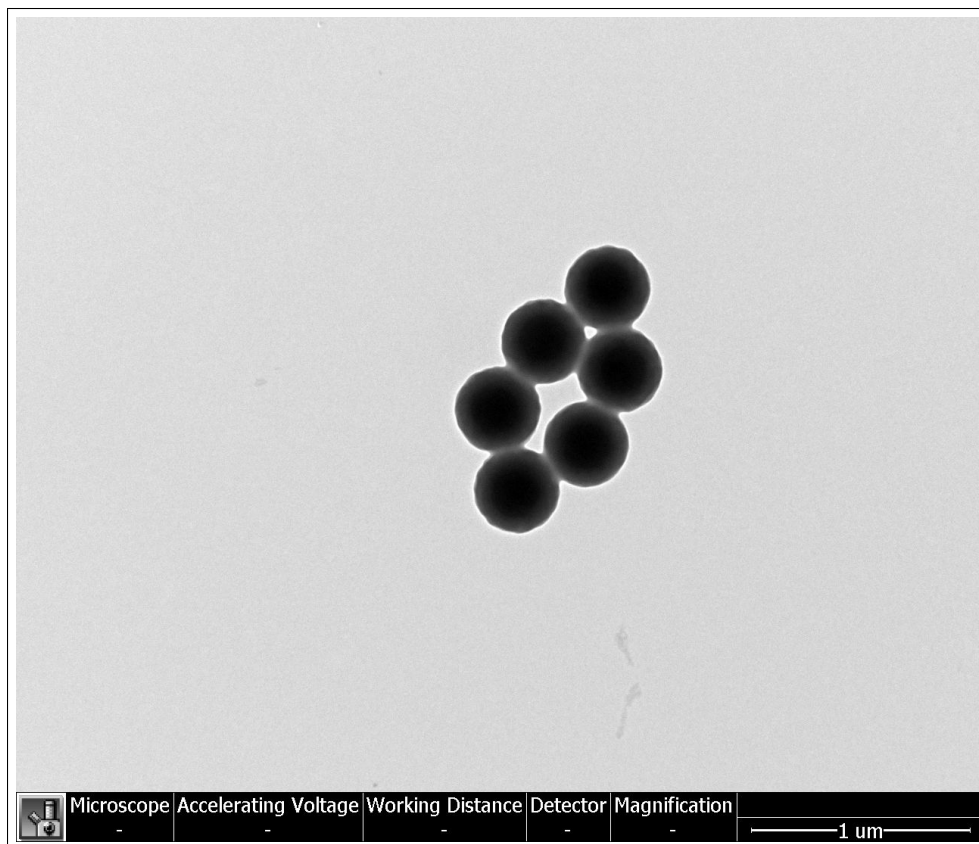
| Sample             | TEM size (d.nm)    | Solid content (%) | Conversion (%) | Aggregation? |
|--------------------|--------------------|-------------------|----------------|--------------|
| PS+07 (I)          | $385.3 \pm 4.79\%$ | 8.06              | 88.7           | A little bit |
| PS+07 (II)         | Aggregation        | 6.57              | 65.1           | A lot of     |
| PS+08 <sup>2</sup> | $390.8 \pm 6.16\%$ | 3.65              | 85.3           | A little bit |

**Table 4.6:** Zetasizer measurements of the positive polystyrene particles, method B

| Sample             | Zetasize backscattering (d.nm) | Zetasize forward scattering (d.nm) | Zetapotential (mV) |
|--------------------|--------------------------------|------------------------------------|--------------------|
| PS+07 (I)          | 418.4                          | 377.5                              | 36.8               |
| PS+07 (II)         | 8811                           | 1101                               | 17.5               |
| PS+08 <sup>2</sup> | 424.0                          | 367.0                              | 23.1               |

<sup>2</sup>The measurements of the sample were done after three hours of centrifugation at 3750 rpm.

Experiment **PS+08** succeeded. The particles are big enough and have the desired charge on the surface (Fig 4.1). PS+08 will be the positive polystyrene particles that are the seeds for the raspberry-like particles.



**Figure 4.1:** TEM image of PS+09 particles.

### Forward scattering

In general, the results from the forward scattering of the Zetasizer were not accurate with respect to the results of the backward scattering (Table 4.3 & 4.6). The particle size that is measured with the Zetasizer have to be **a little bit larger** than the particle size measured with the TEM (not almost twice as large, PS+05 Table 4.2 & 4.3). This is because the TEM measures a particle size of dried particles and the Zetasizer measures a particle size of particles in solution (hydrodynamic size). The backward scattering is more reliable with this than the forward scattering.

Furthermore, it was mentioned before in Section 2.4 that there is a difference in forward scattering and backward scattering. Large particles scatter the light especially forwards and small particles scatter the light everywhere. This is exactly the reason why the forward scattering result from PS+08 (step 2) is the most accurate from all the forward scattering results. This sample had a lot of aggregation, so the particles are larger in size. This resulted in a more accurate result. This is also why the result from the back scattering is not accurate. Because the small particles besides this seed particles have to be measured too, the Zetasizer setting will be set on only the backward scattering.

### pNIPAM

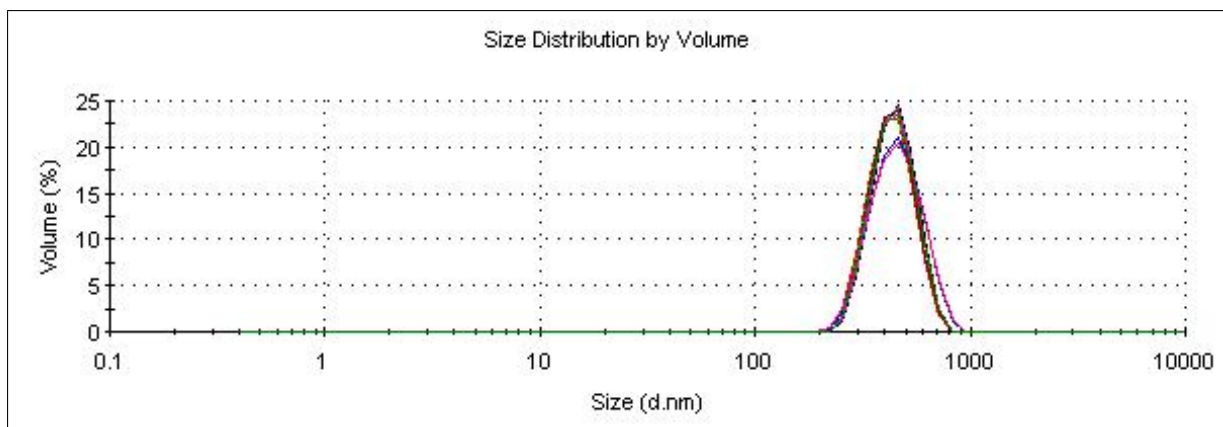
PS+09 contains 10% wt pNIPAM and it is known that pNIPAM shrinks with increasing temperature ( $\sim 30^{\circ}\text{C}$ ). Before the measurement with the TEM, a droplet of the sample is dried under a halogen lamp. Therefore, it is possible that the size of the dried particles is smaller than the

size of the particles in dispersion. This is why a temperature test needs to be done on PS+09 to see if NIPAM influences the size in dispersion. A diluted sample of PS+09 is measured with the Zetasizer utilizing a temperature program (Table 4.7).

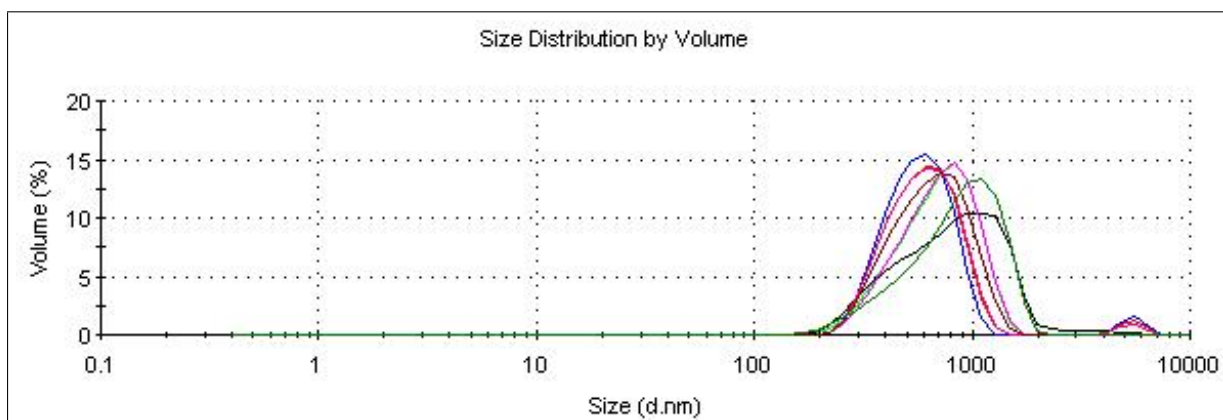
The size distribution is the distribution of the particle size that is measured of all the runs in one measurements at a certain temperature. Therefore, the particle size is named the average size because it is the average size of all the runs. The size distribution can be judged as good or as bad. When a sample does not aggregate it will remain the same during the measurement and a size distribution like Fig 4.2a could be expected. When a sample does aggregate it will not remain the same during the measurement and a size distribution like Fig 4.2b could be expected. It can be concluded that there is no aggregation in PS+09 because in the beginning, in the middle and in the end of the temperature measurement test, the size distribution of most measurements is good. The expected particle size is approximately 424 d.nm (Table 4.6). When a large particle size is measured, the size distribution is bad. This can not be due to aggregation, because the measured size that is larger is not twice the size of one particle. Furthermore, it is remarkable that the size distribution of the first measurement at 5°C is good and the second is bad while the temperature remains at 5°C. Therefore, the results with a bad size distribution are neglected and the results in the circle remains (Fig 4.2c). It can be concluded that the amount of pNIPAM seems to be not enough to introduce temperature dependent particle size in PS+09 (in a temperature range from 5 to 45°C).

**Table 4.7:** Temperature dependent test of PS+09 with the Zetasizer

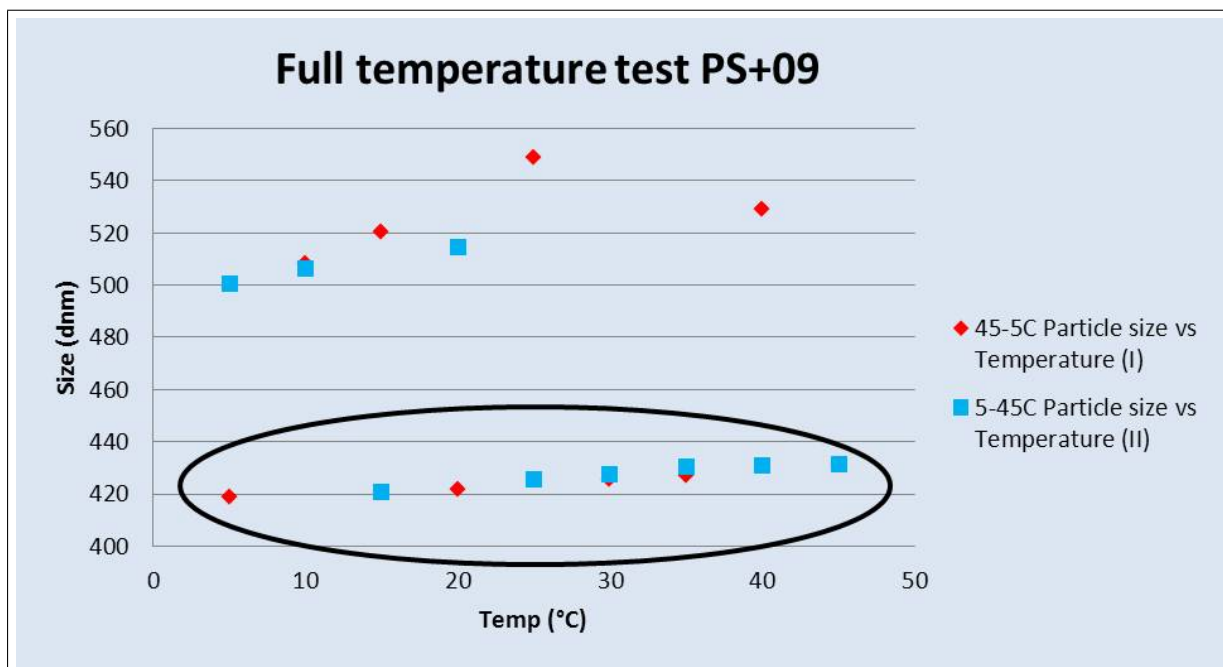
| Temperature (°C) | Average size (d.nm) | Size distribution |
|------------------|---------------------|-------------------|
| 45               | 431.6               | good              |
| 40               | 529.1               | bad               |
| 35               | 427.0               | good              |
| 30               | 425.5               | good              |
| 25               | 548.7               | bad               |
| 20               | 421.6               | good              |
| 15               | 520.6               | bad               |
| 10               | 508.3               | bad               |
| 5                | 419.0               | good              |
| 5                | 500.4               | bad               |
| 10               | 506.5               | bad               |
| 15               | 420.9               | good              |
| 20               | 514.4               | bad               |
| 25               | 425.4               | good              |
| 30               | 427.5               | good              |
| 35               | 430.2               | good              |
| 40               | 430.8               | good              |
| 45               | 431.2               | good              |



(a)



(b)



(c)

**Figure 4.2:** Figure (a) shows a relatively good volume% size distribution at 5°C, the first measurement. Figure (b) shows a relatively bad volume% size distribution at 5°C, the second measurement. Figure (c) shows the temperature dependency of NIPAM in PS+09. The red line of 1A was carried out first and after that the blue line 1B was measured. This was done in one measurement.

## 4.2 Results of Negatively Charged Polystyrene Particles

The negative polystyrene particles (PS-01) were provided by a colleague. The synthesis of the negative polystyrene particles is described in the experimental section (Section 3.2). The synthesis results of PS-01 are given in Table 4.8. This sample is not centrifuged.

**Table 4.8:** Characterizations of PS-01

| Sample                         | PS-01             |
|--------------------------------|-------------------|
| TEM size (d.nm)                | $80.9 \pm 10.7\%$ |
| Zetasize backscattering (d.nm) | 87.9              |
| Zetapotential (mV)             | -52.2             |
| Solid content(%)               | 7.22              |

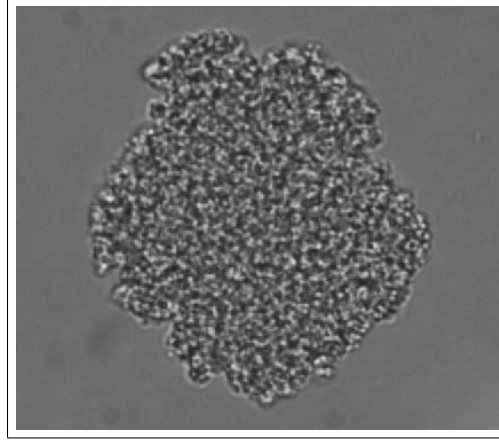
## 4.3 Results of Raspberry-like Particles

The goal of this project is to obtain raspberry-like particles. Equation 2.3.1 (that calculates the coverage of small silica particles onto large sterically stabilized poly(2-vinylpyridine) latex particles in aqueous solution) is used as starting point to calculate the amounts of positive and negative particles that need to be added together for raspberry-like particles. Furthermore, a value for the solid content and a value for the coverage amount have to be chosen. After consultation these values were set on: 2% SC<sub>s</sub> (Solid Content small particles), 2% SC<sub>l</sub> (Solid Content large particles) and a coverage of 80%. These values can be adapted depending on the results. Since also the radii are known for the small and large particles, the amount of small particles onto the surface of one large particle were calculated. Equation 2.3.1 results in  $N \cong \frac{4 * P * (r_l + r_s)^2}{r_s^2}$ . The ratio small:large particles becomes approximately 100:1. Utilizing the solid contents of the dispersions, the quantities were calculated. To improve the coverage, salt was added. The range of the chosen salt concentrations that was added were based on an article of Harley<sup>[1]</sup>. Table 4.9 shows the conditions.

**Table 4.9:** The conditions for 2%SC raspberry-like particles

| Solution/dispersion    | Tube 1 (mL) | Tube 2 (mL) | Tube 3 (mL) |
|------------------------|-------------|-------------|-------------|
| PS+09                  | 5.479       | 5.479       | 5.479       |
| PS-01                  | 2.500       | 2.500       | 2.500       |
| NaCl (1M)              | 1.000       | 0.100       | X           |
| NaCl (0.1M)            | X           | X           | 0.100       |
| Milli-Q water          | 1.021       | 1.921       | 1.921       |
| Total volume           | 10.00       | 10.00       | 10.00       |
| Salt concentration (M) | 0.1         | 0.01        | 0.001       |

After 24 hours of mixing, there was some aggregation visible in the tubes. Investigation with the optical microscope confirmed this (Fig 4.3). Harley reported no aggregation, so it can not be caused by the salt concentration. It could be that the solid content is too high for the system. Therefore, the next raspberry-like particles will contain 1%SC. Furthermore, the sample volumes will be smaller in order to use less material. Table 4.10 shows the conditions for the



**Figure 4.3:** This is a image of PS+09 + PS-01 in 0.001M NaCl and based on 2%SC. The picture is made with an optical microscope (zoom: 100X/<sub>130oil</sub>).

1%SC raspberry-like particles.

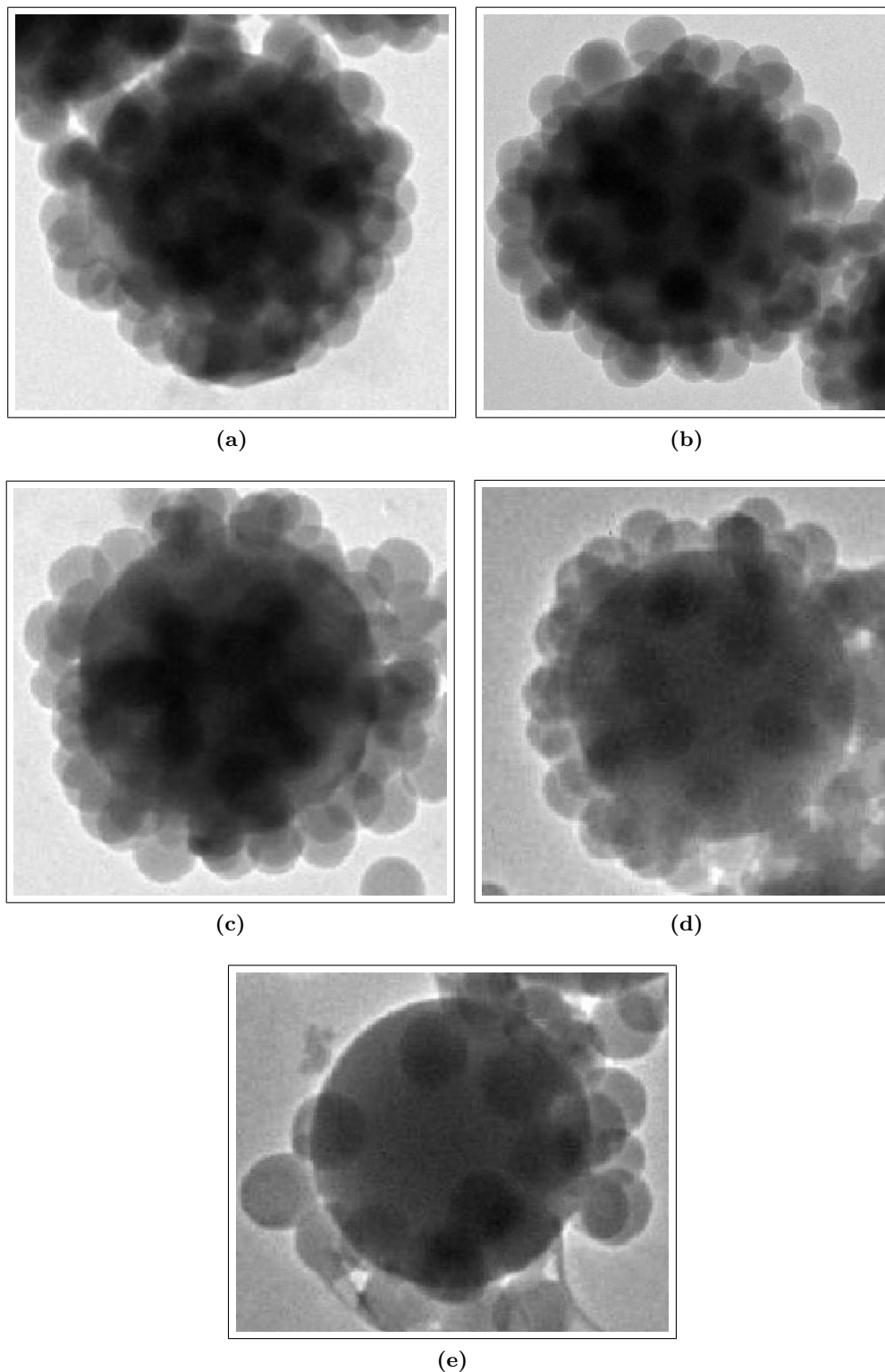
**Table 4.10:** The conditions for 1%SC raspberry-like particles

| Solution/dispersion    | Tube 4 (mL) | Tube 5 (mL) | Tube 6 (mL) | Tube 7 (mL) | Tube 8(mL) |
|------------------------|-------------|-------------|-------------|-------------|------------|
| PS+09                  | 1.096       | 1.096       | 1.096       | 1.096       | X          |
| PS+05                  | X           | X           | X           | X           | 1.394      |
| PS-01                  | 0.614       | 0.614       | 0.614       | 0.614       | 0.809      |
| NaCl (1mM)             | 0.400       | X           | X           | X           | 0.400      |
| NaCl (0.1M)            | X           | 0.400       | X           | X           | X          |
| NaCl (0.01M)           | X           | X           | 0.400       | X           | X          |
| Milli-Q water          | 1.890       | 1.890       | 1.890       | 2.290       | 1.397      |
| Total volume           | 4.000       | 4.000       | 4.000       | 4.000       | 4.000      |
| Salt concentration (M) | 0.100       | 0.010       | 0.001       | 0.000       | 0.100      |

Samples were taken from Tube 4 to 6 and the samples were checked under the optical microscope. There was no aggregation visible after 24 hours of mixing. To look at the system in more detail, three samples were prepared for the TEM. In Fig 4.4a, 4.4b and 4.4c can be seen that the coverage decreases with decreasing salt concentration when the focus is on the edges of the seed particles. Harley saw the same salt concentration dependency<sup>[1]</sup>.

It can be concluded that the heterocoagulation technique works. To give a better view of the system, two control experiments will be preformed. One control experiment is to see if raspberry-like particles can be formed without salt (Tube 7). The sample was prepared for TEM and imaged with it (Fig 4.4d). It can be seen that raspberry-like particles are formed without salt, but with a lower coverage than the salt containing samples.

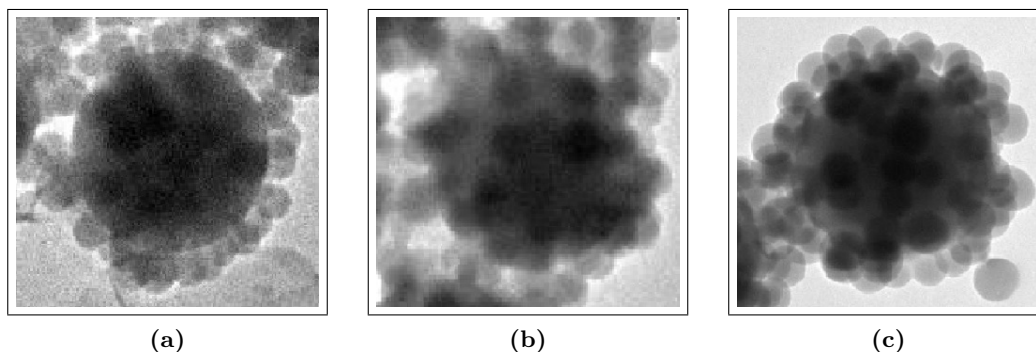
The other control experiment is based on the knowledge that pNIPAM adsorbs readily on polystyrene. This might cause better adhesion. Therefore, a sample without pNIPAM was made (Tube 8). The sample was prepared for TEM and imaged with it. It can be seen that the coverage is very low or even nothing (4.4e). Therefore, there can be conclude that the presence of pNIPAM (co-polymerized with styrene) is important for the formation of raspberry-like particles.



**Figure 4.4:** Image (a) to (e) are close-ups of the TEM images in Figure A.1 to A.5 (respectively) in the Appendix. Image (a) is from Tube 4 (0.1M NaCl), image (b) is from Tube 5 (0.01M NaCl), image (c) is from Tube 6 (0.001M NaCl) and image (d) is from Tube 7 (without NaCl). When the focus is on the edges of the seed particles, there is an increase in the visibility of it (from (a) to (d)). This means that the coverage decreases with decreasing salt concentration. Figure (e) is a TEM image of Tube 8 (0.1M NaCl and without pNIPAM), where the edge of the seed particle is clearly visible. Therefore, pNIPAM has a good influence on the forming of raspberry-like particles.

### Mixing time

In all experiments so far, the mixing time was 24 hours. This is relatively long and therefore it is useful to know how long the samples have to be mixed. An experiment is performed to see if the coverage does equilibrate over time. Therefore, Tube five is made again and a sample was taken directly after mixing, after 2 hours and after 24 hours. TEM images were made and can be seen in Figure 4.5a, 4.5b and 4.5c. It can be seen that there is an increase in coverage over time, because the edges of the particles decrease in visibility from 0 hours mixing to 24 hours mixing. Figure 4.5b is difficult to judge because the resolution is relatively bad. However, the images in Figure A.6 to Figure A.8 in the Appendix show an increase in free (small) particles. There can be concluded that the coverage increases over time. Maybe there exists a coverage optimum between 2 hours mixing and 24 hours mixing.



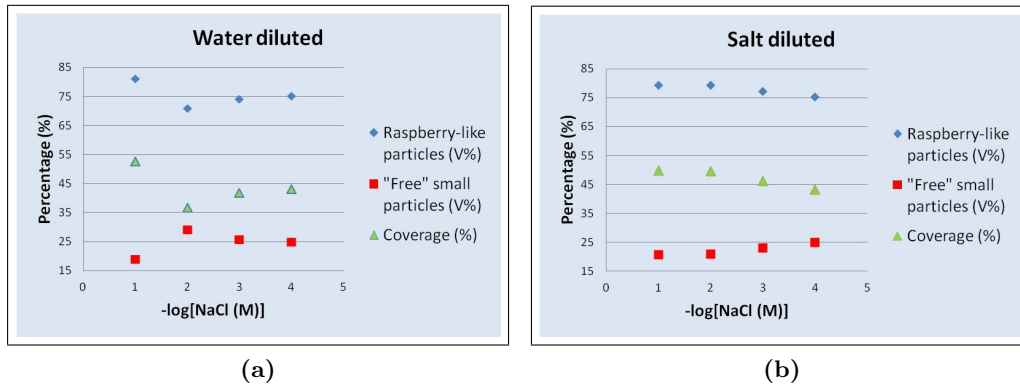
**Figure 4.5:** Image (a) to (c) are close-ups of the images in Figure A.6 to A.8 (respectively) in the Appendix. It can be seen that there is an increase in coverage over time, because the edges of the particles decrease in visibility from 0 hours mixing (a) to 24 hours mixing (c). Image (b) is difficult to judge because the resolution is relatively bad. However, the images in Figure A.6 to Figure A.8 in the Appendix show an increase in free (small) particles.

### Determining a value for the coverage

The visibility of the edges from the seed particles (from TEM images) are an assessment point for the coverage. Therefore, it is not convenient to compare several coverages with each other when the conditions differs. The coverage can be compared with each other on a more convenient way when the coverage is expressed with a value. Therefore, an experiment was performed to see if a value can be found for the coverage.

Since there is no coverage of 100%, there are raspberry-like particles and free small particles in the dispersion. The Zetasizer should measure this and detect two signals, one for the raspberry-like particles and one for the free (small) particles. The Zetasizer can calculate a size distribution from these signals, expressed in volume percent. As seen before, the coverage is higher when the salt concentration is higher and therefore there are less free particles in dispersion. This should give a relation between the volume percent of free particles and the salt concentration. This is why an experiment with the Zetasizer was performed.

Tube 4 to Tube 7 from Table 4.10 were made again for the experiment. A good approximation for the salt concentration in the sample with no salt is  $10^{-4}M$  (Tube 7), because water contains always a small amount of salt. When the salt concentration is higher, a size distribution where the volume percent of free small particles is lower would be expected (Fig 4.6a). Unfortunately, the Zetasizer showed no logical relation, because the coverage from the sample that contains  $0.001M$  NaCl is higher with respect to the sample that contains  $0.01M$  NaCl. The reason for this could be that the samples were diluted with the wrong dispersant (before the measurement). Approximately one droplet was taken from these samples and this was diluted with water. Therefore,



**Figure 4.6:** This figure shows an increase in raspberry-like particles and a decrease in "free" small particles with increasing salt concentration. A good approximation for the salt concentration in the sample with no salt is  $10^{-4}M$ , because water contains always a small amount of salt.

the salt concentration in the sample is also diluted and this changes the Debye-length and thus the covering. Not every droplet is diluted in the same amount of water, so maybe that this could explain the higher coverage of the  $0.001M$  NaCl sample. To prevent this, the samples can be diluted with the corresponding salt concentration so the particles are kept in the same environment. Fig 4.6b shows the result. This is the relation that was expected and therefore the Zetasizer can be used to determine a value for the coverage.

This value is expressed in a volume percent and the volume percent free (small) particles can be calculated to a number of **Free Particles** ( $FP$ , Appendix 2). The same can be done for the **Total number Seed Particles** ( $TS_{eedP}$ ). Since the **Total number of Small Particles** ( $TSP$ ) is known, the total number of **Small Particles On the surface of the Seed Particles** is also known:  $SPOSP = TSP - FP$ . The total number of  $SPOSP$  divided by  $TS_{eedP}$ , equals to  $N$  in equation 2.3.1. Finally, the coverage was calculated with this equation (Table 4.11).

**Table 4.11:** An overview of coverage difference from raspberry-like particles

| Salt concentration ( $M$ ) | Volume% small particles | Coverage (%) |
|----------------------------|-------------------------|--------------|
| $1.0 * 10^{-1}$            | 20.7                    | 49.8         |
| $1.0 * 10^{-2}$            | 20.9                    | 49.5         |
| $1.0 * 10^{-3}$            | 23.0                    | 46.2         |
| $1.0 * 10^{-4}$            | 24.9                    | 43.2         |

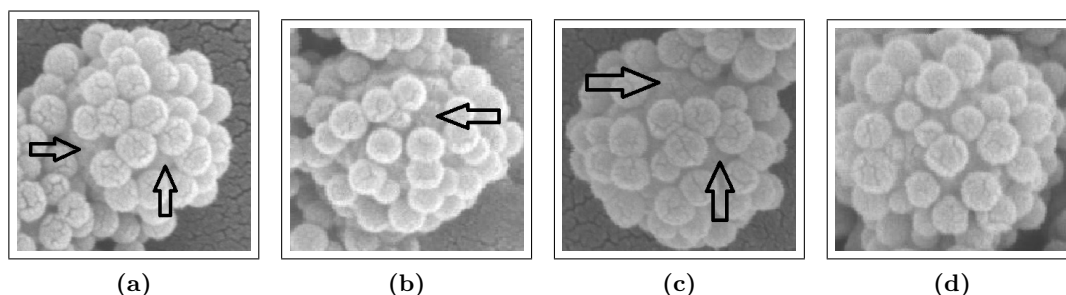
The difference in coverage percentages are significantly smaller from  $0.1M$  NaCl to the sample with no salt ( $\sim 7\%$ ) than the differences in the pictures of the TEM (respectively Fig 4.4a to 4.4d). Therefore, the Zetasizer results can not be used for quantitative purposes but it can be used for qualitative purposes.

#### Water diluted or salt concentration diluted dependent for the coverage

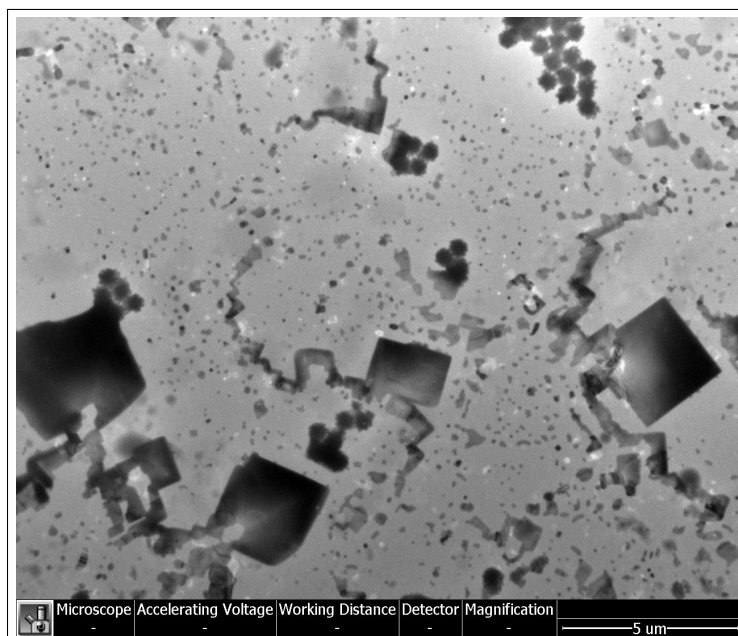
As mentioned above, there is a significant difference in the coverage for the observed samples that were diluted with water or with the corresponding salt concentration. The reason for this is also explained. Therefore, the conclusion is that the best way of diluting the samples is done with the corresponding salt concentration (this were the expected results). However,

this conclusion is based on TEM images (judged on a 2D view) and on Zetasizer measurements (a qualitative analysis). Therefore, an extra experiment was performed to control this conclusion.

For this experiment Tube 4 and Tube 5 were made again and investigated with the SEM. The SEM was chosen because this shows a "3D" view of the raspberry-like particles and this gives a better view of the coverage. SEM images shows that the coverage is better and more distributed when the samples are diluted salt dependent (Fig 4.7a to 4.7d). Therefore, this experiment can confirm the above conclusion. Furthermore, it is known for sure that this is the salt concentration that the particles are feeling. However, the disadvantage is that the TEM images can contain salt crystals at higher salt concentrations (Fig 4.8).



**Figure 4.7:** Image (a) to (d) are close-ups of the images in Figure A.9a to A.9d (respectively) in the Appendix. The arrows in the images points to the bare spots. It is a bit difficult to see but image (a), Tube 4 diluted with water, has more bare spots with respect to image (b), Tube 4 diluted with 0.1M NaCl. Furthermore, the bare spots of (b) are better distributed. The same can be seen with image (c), Tube 5 diluted with water, compared with image (d), Tube 5 diluted with 0.01M NaCl. However, the differences are more easy to see here.



**Figure 4.8:** TEM image of a raspberry-like particle dispersion which contains a relative high salt concentration, 0.1M NaCl. The squares are salt crystals.

### Sequence of adding dispersions together

It is useful to find out if the sequence of adding everything together matters for the forming of raspberry-like particles. If it does not matter, there is an equilibrium and the properties of the raspberry-like particles will depend only on the final conditions. Two important points that can make a difference is when the particles feel the salt concentration and when the positive particles meet the negative particles. Therefore, an experiment was performed where the sequence of adding everything together differs (Table 4.12).

**Table 4.12:** Raspberry-like particles conditions of 1%SC raspberry-like particles. The addition sequence differs.

| #              | Solution/dispersion (mL)                | 0.1M NaCl | 0.01M NaCl |
|----------------|-----------------------------------------|-----------|------------|
| 1              | PS+09                                   | 1.096     | 1.096      |
| 2              | PS-01                                   | 0.614     | 0.614      |
| 3              | NaCl (1M)                               | 0.400     | X          |
| 4              | NaCl (0.1M)                             | X         | 0.400      |
| 5              | Milli-Q water                           | 1.890     | 1.890      |
| A <sup>3</sup> | 3+5, mix, +1, mix, +2, mix for 24 hours |           |            |
| B              | 3+5, mix, +2, mix, +1, mix for 24 hours |           |            |
| C              | 2+1, mix, +5, mix, +3, mix for 24 hours |           |            |
| D              | 3+2, mix, +1, mix, +5, mix for 24 hours |           |            |

After 24 hours of mixing, measurements with the TEM and Zetasizer were done. The coverage percentage or the volume percent from the Zetasizer can be used because it is for a qualitative purpose. The Zetasizer detected in some cases three signals; free small particles, large raspberry-like particles and larger clusters. The size distribution in volume% (V%) are given in Table 4.12.

**Table 4.13:** Results of the addition sequence test

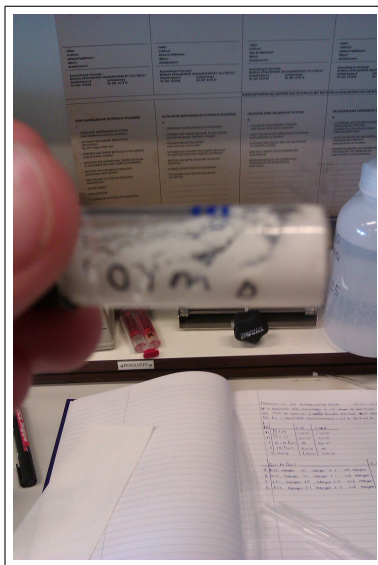
| Sample    | Raspberry-like particles (V%) | Small particles (V%) | Clusters (V%) | Coverage percentage (%) | Visual coverage (TEM) |
|-----------|-------------------------------|----------------------|---------------|-------------------------|-----------------------|
| A (0.1M)  | 77.4                          | 20.6                 | 2.00          | 49.9                    | +                     |
| B (0.1M)  | 60.4                          | 39.6                 | 0.00          | 20.3                    | +                     |
| C (0.1M)  | 46.0                          | 54.0                 | 0.00          | 0.00                    | ±                     |
| D (0.1M)  | 100                           | 0.00                 | 0.00          | X                       | +                     |
| A (0.01M) | 85.5                          | 11.9                 | 2.30          | 63.5                    | ±                     |
| B (0.01M) | 60.7                          | 37.8                 | 1.50          | 23.1                    | ±                     |
| C (0.01M) | 46.2                          | 44.1                 | 9.70          | 13.2                    | +                     |
| D (0.01M) | 75.3                          | 24.7                 | 0.00          | 43.5                    | +                     |

It can be seen that there is no equilibrium reached after 24 hours mixing, because the results differs from each other. Therefore, it is shown that the sequence of adding everything together does matter (with a mixing time of 24 hours). The results with the highest coverage percentage is the best. Therefore, method "A" is the best sequence to add everything together. This can be explained. With respect to method "B", the last step was the addition of small particles. It could be that small particles can move more easily through the dispersion than the large particles. Therefore, the small particles can fill up the bare spots. The other difference between

<sup>3</sup>For the samples with 0.01M NaCl, number 3 is replaced by number 4.

method "A" and "B" is the volume percentage clusters. It could be that method "A" contains more clusters through bridging, because the seed particles can be closer to each other after mixing with salt and water. With method "B" the seed particles can bridge less with each other, because the seed particles are mixed with negatively charged particles, salt and water. With method "C" the positively and negatively charged particles get a salt shot (1M) compared to method "A". Therefore, the particles do not feel the same salt concentration everywhere in the beginning. This causes a relatively low coverage.

Method "D" developed direct coagulation after adding negatively charged particles to 0.1M NaCl (Fig 4.9). This was not observed with 0.01M NaCl. Therefore, method "D" is not a good sequence for mixing everything together in general with respect to method "A".



**Figure 4.9:** This is the result of sample D after adding negatively charged particles to 0.1M NaCl.

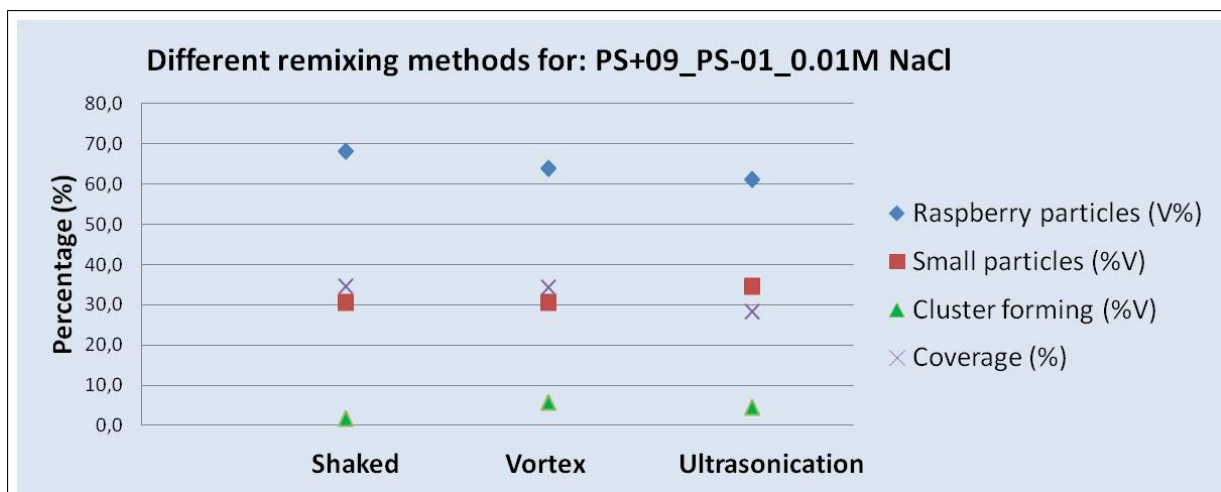
The TEM images of the 0.1M sample from table 4.12 can be seen in Figures A.10a to A.10d (Appendix). Image A.10a to A.10d corresponds to the different addition order "A" to "D". The difference between A.10a and A.10b are difficult to see. However, image A.10c is less covered than A.10a and A.10b. Image A.10d shows cluster formation. Therefore, these results correspond reasonably well with the results from the Zetasizer.

The TEM images of the 0.01M sample from table 4.12 can be seen in Figure A.11a to A.11d. Image A.11a to A.11d corresponds again to the different addition order "A" to "D". The difference between the images is hard to see. However, image A.11c has a remarkable number of free particles, which implies a lower coverage. Therefore, these results correspond also reasonably well with the results from the Zetasizer.

In general the results from the TEM images correspond reasonable well with the results from the Zetasizer. However, the TEM images in Figure A.10a to A.10d and Figure A.11a to A.11d showed a better coverage than the results from the Zetasizer. Furthermore, sometimes the difference are difficult to see. This could be due a drying effect. The droplet on the substrate lies under a halogen lamp. During drying, the free small particles can be clustered around the large particles due to capillary forces (the result can look better).

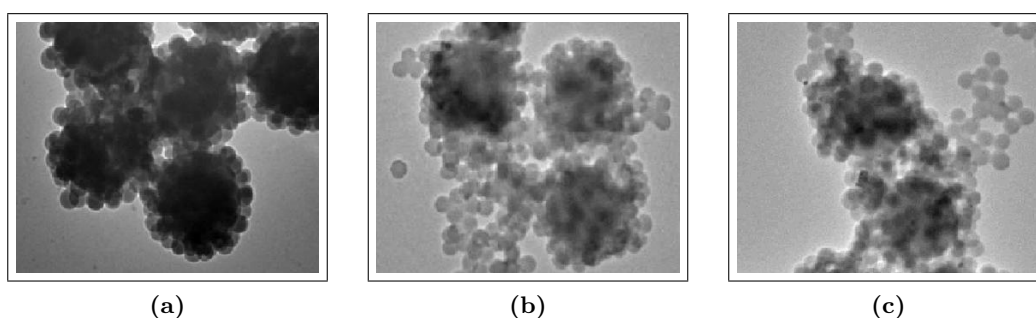
### Stability test

After preparing the raspberry-like particles, it was seen that sedimentation took place when the samples stood still (after  $\sim 3$  days). It is interesting to find out if there is an equilibrium in the system of raspberry-like particles. If the samples are redispersed and the raspberry-like particles are formed back again, there is an equilibrium. Three different methods were used to



**Figure 4.10:** This figure shows a decrease in raspberry-like particles and coverage, an increase in "free" small particles and an increase in cluster forming when the remix method is more robust.

redisperse the samples: by shaking gently, by vortex and by ultrasonication. The duration of redispersing was as long as needed until the sedimentation was no longer visible. The (change in) coverage was investigated using TEM. In addition, the size of the (raspberry-like)-particles was measured with the Zetasizer (back scattering). The expected result is that when the raspberry-like particles are not really stable, the coverage will decrease when the redispersing method is more robust. Therefore, the Zetasizer measures particles with different sizes and thus more peaks are expected. It is also expected that the particle size distribution (volume percent) and thus the coverage percentage of the different peaks changes. This expectations are confirmed by the Zetasizer measurements (Fig 4.10), just like the TEM images (Fig 4.11a to 4.11c). Therefore, the resulting coverage does depend on the redispersing method.



**Figure 4.11:** Image (a) to (c) are close-ups of the images in Figure A.12a to A.12c (respectively) in the Appendix. From (a) to (c) the coverage decreases and the free (small) particles increases.



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# Conclusion & Outlook

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### CONCLUSION

Positive seed particles are polymerized using styrene, AIBA and NIPAM. Negative small particles that should form the roughness of the raspberry-like particle are polymerized using styrene, DVB and SDS. On the basis of the TEM, the seed particles are 390.8 d.nm and the small particles are 80.93 d.nm. The zetasizer measured a zeta potential of 23.1mV for the seed particles and -52.2mV for the small particles. The amount of pNIPAM that the seed particles contain is too low to make the size of the seed particles temperature dependent.

Raspberry-like particles were synthesized with the particles mentioned above. The solid content has to be set on approximately 1% because it was shown that 2% solid content resulted in coagulation of the particles. It was proven that the coverage decreases with decreasing salt concentration (Fig A.1 to A.4). Furthermore, it was also proven that the presence of pNIPAM is essential for the forming of raspberry-like particles, because without pNIPAM the coverage is naught (Fig A.5).

It was been proven that 2 hours mixing is too short because the coverage is higher after 24 hours. Furthermore, there are less free particles left after 24 hours mixing (Fig A.6, A.7 and A.8). Therefore, the mixing time needs to be 24 hours.

A coverage value was not successfully determined for quantitative purposes. However, this investigation provided information on the manner of diluting the samples. When salt is added to the raspberry-like particles, the samples can best be diluted with the corresponding salt concentration so the particles preserve the environment. Furthermore, it is known for sure which salt concentration the particles feel and that this concentration remains (Fig A.9).

To get an optimal coverage, the sequence of adding everything together is important. It has been proven that the best addition order: salt + water, mixing, + large particles, mixing, + small particles, mixing. This has to do with the moment when the small particles or the seed particles come in contact with a certain salt concentration (Fig A.10 and Fig A.11).

The raspberry-like particles cannot be stored for a long time, because after approximately 3 days sedimentation is visible. Redispersing can be done best by shaking gently, because more vigorous redispersing methods lead to more formation of clusters. Furthermore, it also leads to a decrease in coverage (Fig A.12a to A.12c).

## OUTLOOK

There are still things than can be investigated in the future as an extension to this study. The salt concentration range can be extended with different concentrations and another maximum and minimum. There are also addition orders left that were not tested. The mixing time can also be optimized, because a wide time range is left between 2 hours and 24 hours. Furthermore, a maximum solid content test can be preformed to find out the maximum value. Than, the different ratios for "small particles" : "large particles" can be tested, to see what the coverage does.

Further things that need to be done (and have a higher priority), is to find a way to quantitatively measure the coverage. Another important point is, try to attach small particles to large particles permanently. This is useful for applications (within FCC). This could be done with sintering.

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# Acknowledgements

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- Everybody else from FCC for the sociability and (often) crazy but very interesting conversation topics during the breaks.
- Tricolore and his cooks for the fine Italian sandwiches.



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# List of Abbreviations

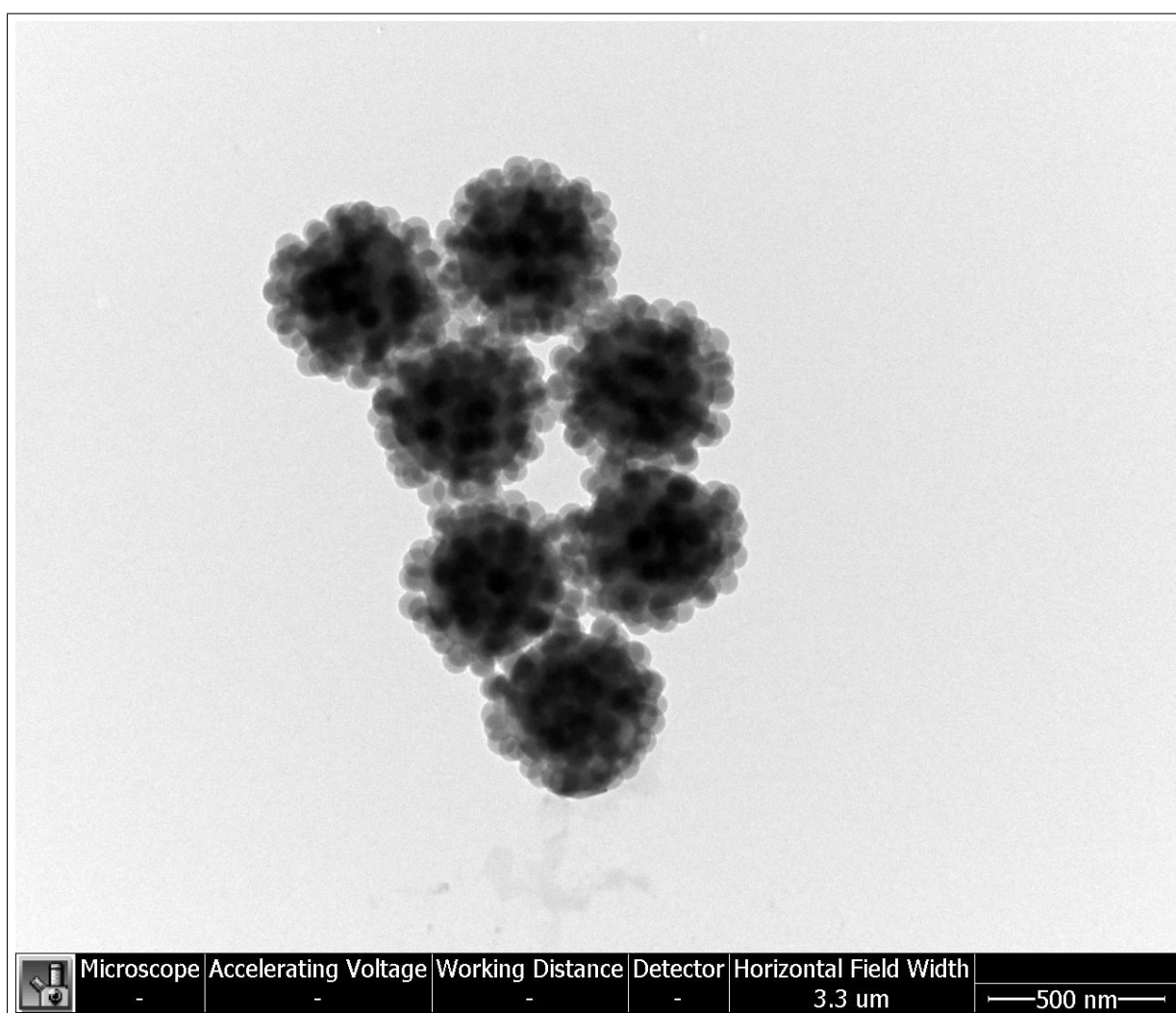
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|                     |                                                      |
|---------------------|------------------------------------------------------|
| $\rho$              | density                                              |
| AEM                 | 2-Aminoethylmethacrylaat hydrochloride               |
| AIBA                | 2,2-azobis(2-methylpropionamide) dihydrochloride     |
| CEC                 | Critical Electrolyte Concentration                   |
| d.nm                | diananometer                                         |
| DVB                 | Divinyl Benzene                                      |
| FCC                 | Physical & Colloid Chemistry                         |
| FP                  | Total number of Free Particles                       |
| KPS                 | Potassium Persulfate                                 |
| MBA                 | Methylenebisacrylamide                               |
| mV                  | millivolt                                            |
| NIPAM               | N-isopropylacrylamide                                |
| r                   | radius                                               |
| rpm                 | rounds per minute                                    |
| SC <sub>l</sub>     | Solid Content large particles                        |
| SC <sub>s</sub>     | Solid Content small particles                        |
| SDS                 | Sodium Dodecyl Sulfate                               |
| SEM                 | Scanning Electron Microscopy                         |
| SP                  | Small Particles                                      |
| SPOSP               | Small Particles On the surface of the Seed Particles |
| TAP                 | Total Amount of Particles                            |
| TEM                 | Transmission Electron Microscopy                     |
| TFFDSEM             | Thin-Film Freeze-Drying Scanning Electron Microscope |
| TS <sub>eed</sub> P | Total number of Seed Particles                       |
| TSP                 | Total number of Small Particles                      |
| V                   | volume                                               |
| wt                  | weight                                               |

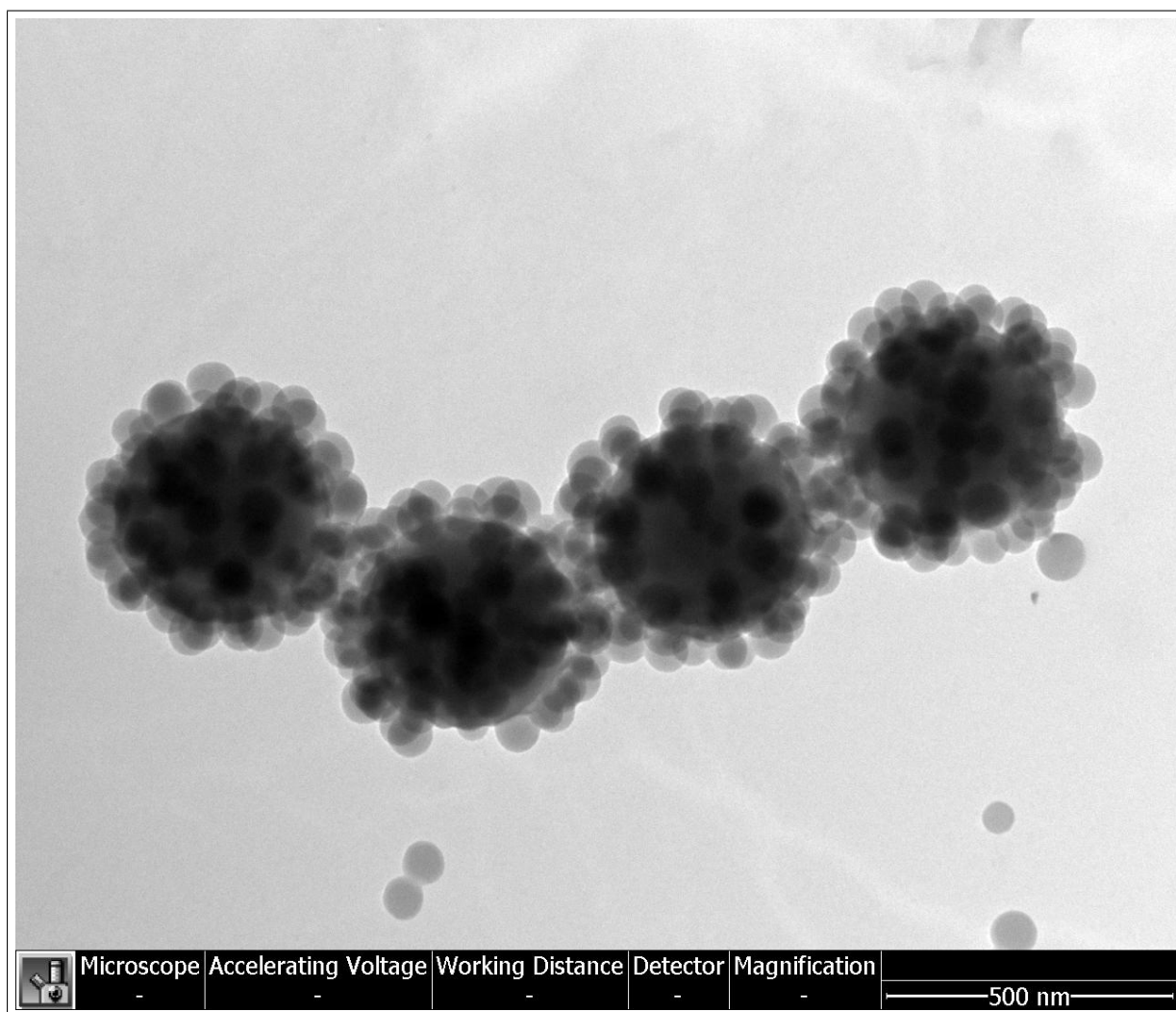


## Appendix A

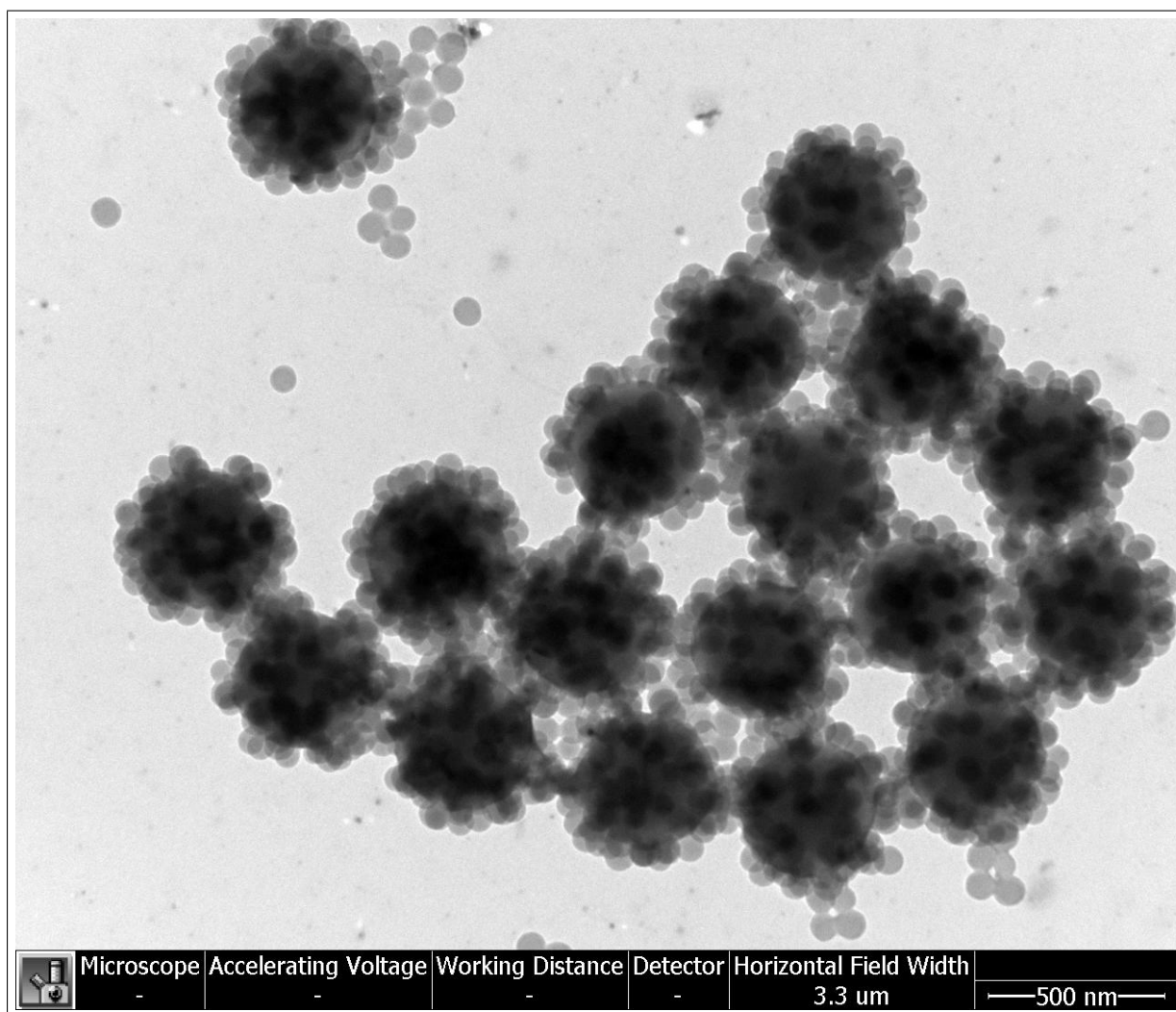
### Figures



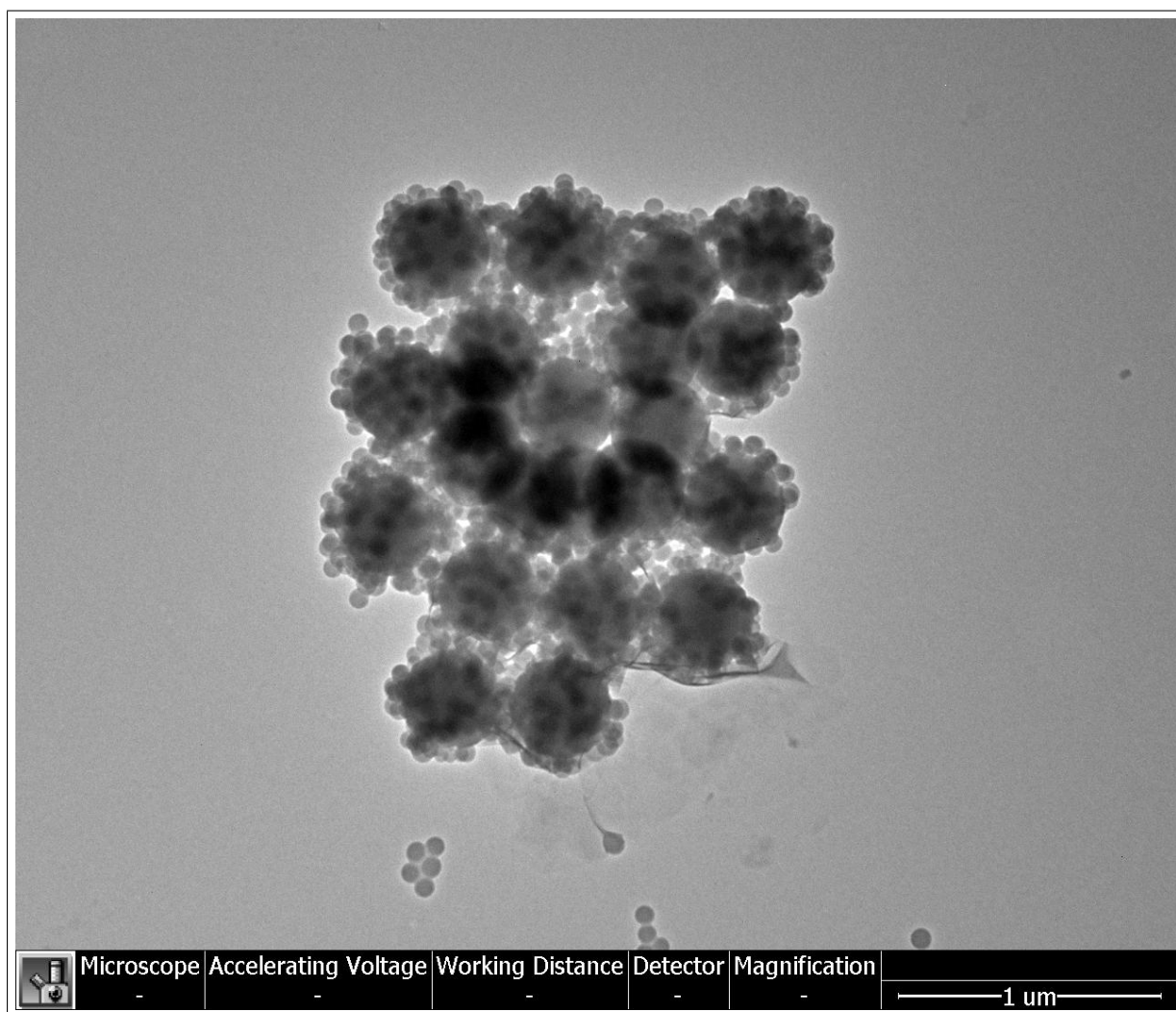
**Figure A.1:** TEM image of tube 4, with 0.1M NaCl. The edges of the seed particles are a bit hard to see.



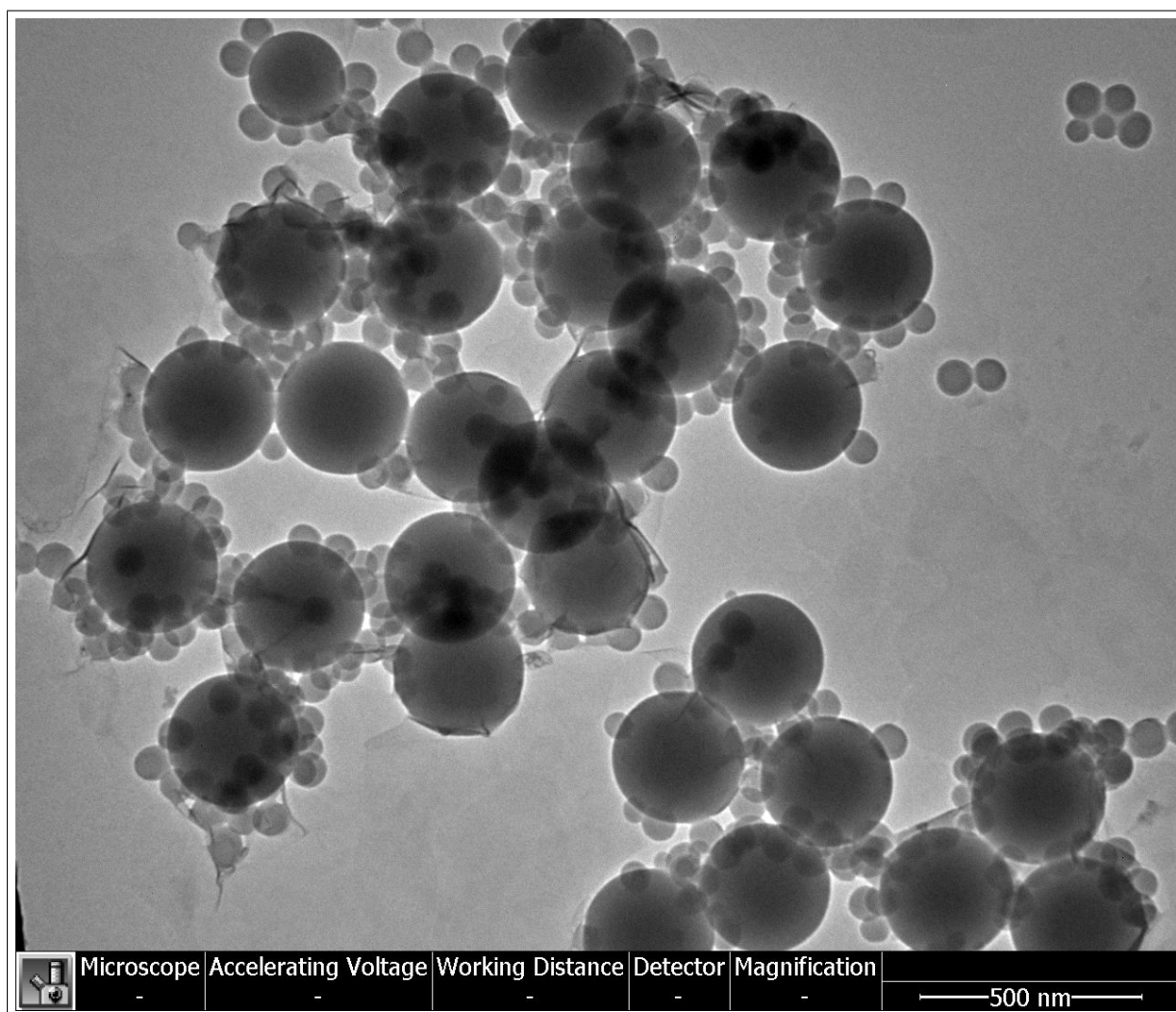
**Figure A.2:** TEM image of tube 5, with 0.01M NaCl. The edges of the seed particles are more easy to see.



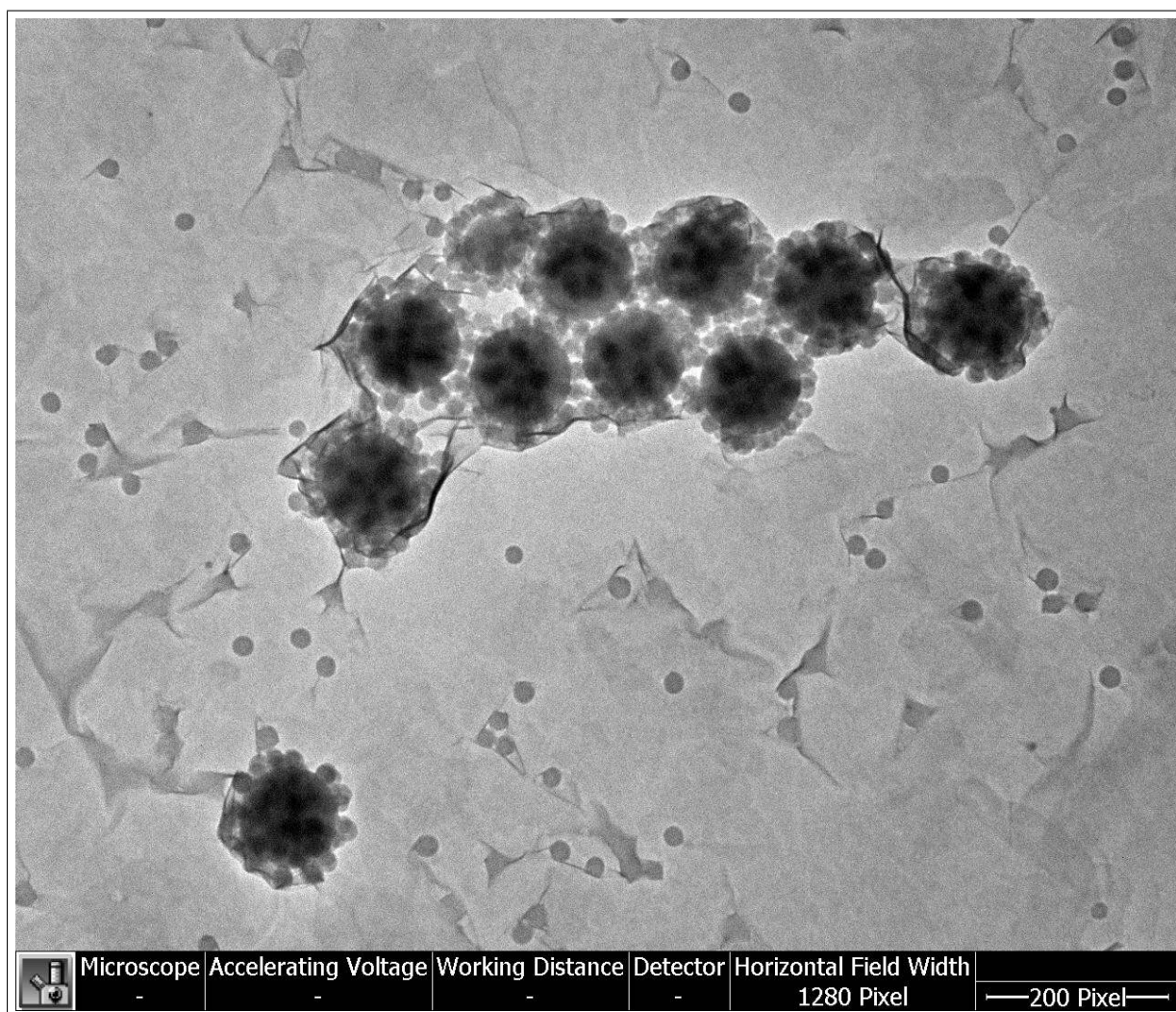
**Figure A.3:** TEM image of tube 6, with 0.001M NaCl. The edges of the seed particles are easy to see. There are even bare spots.



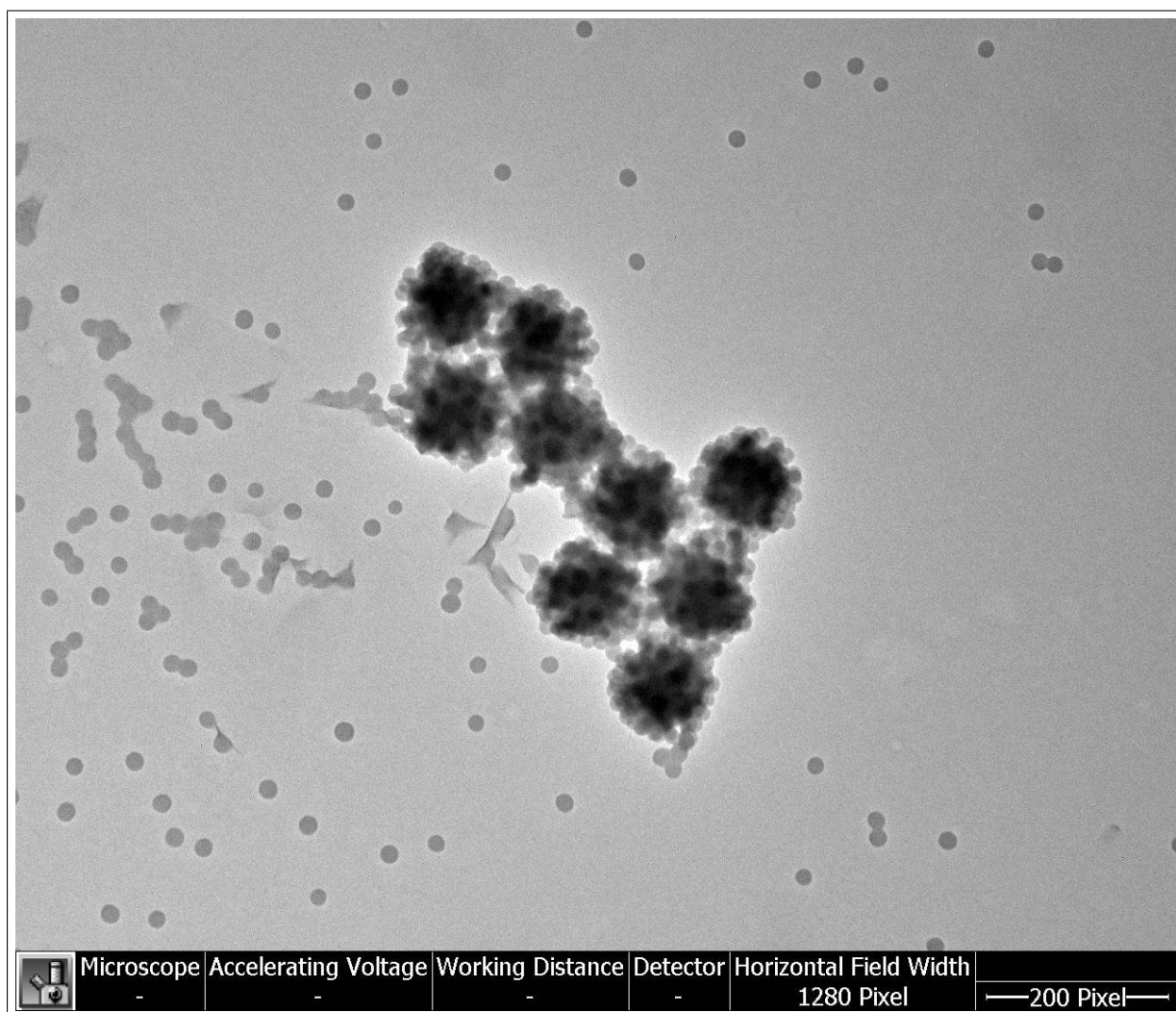
**Figure A.4:** TEM image of tube 7, without NaCl. The edges of the seed particles are easy to see. There are even bare spots and "free" particles.



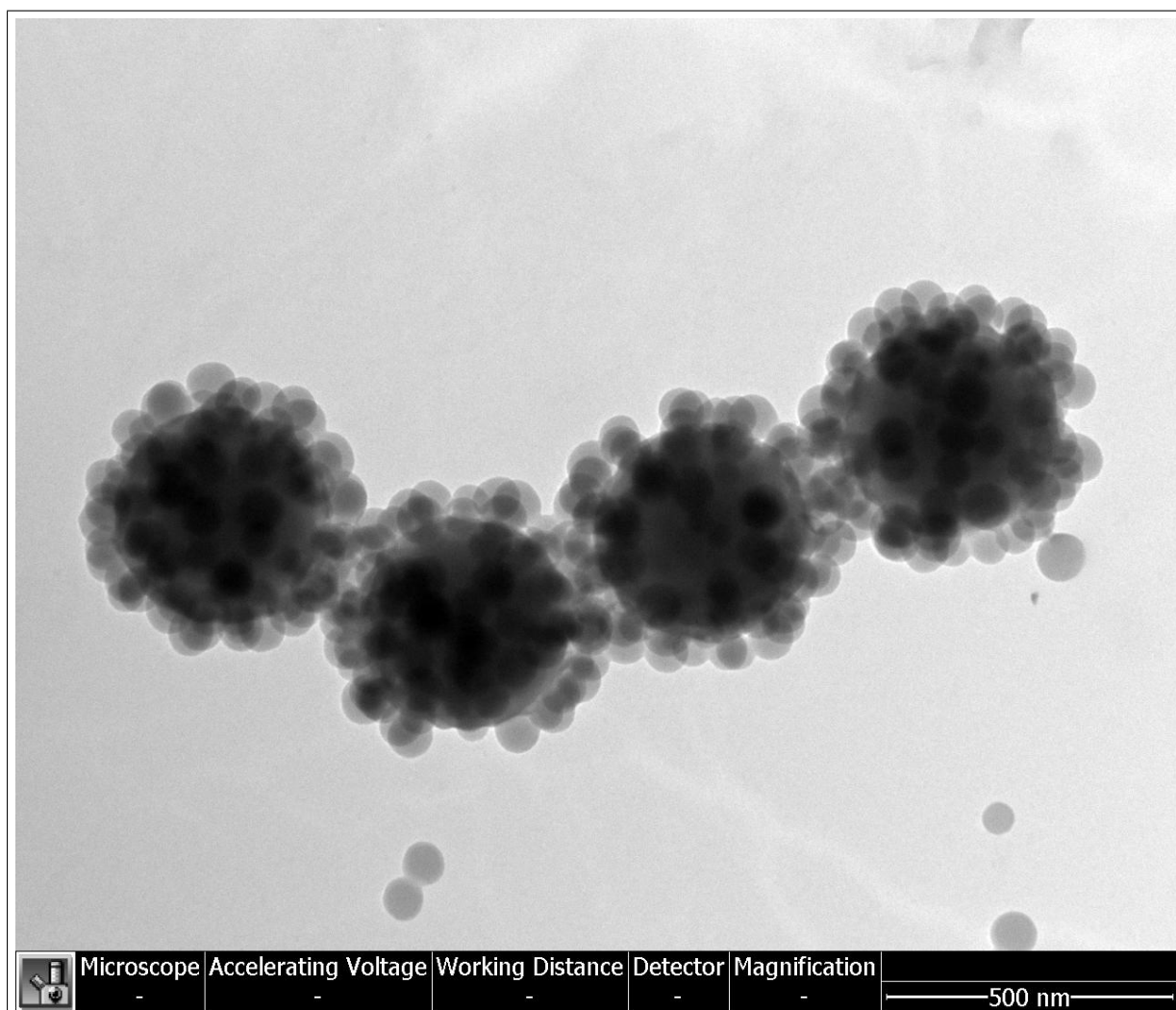
**Figure A.5:** TEM image of tube 8, with 0.1M NaCl and without NIPAM. The small particles are barely on the surface of the large particles anymore.



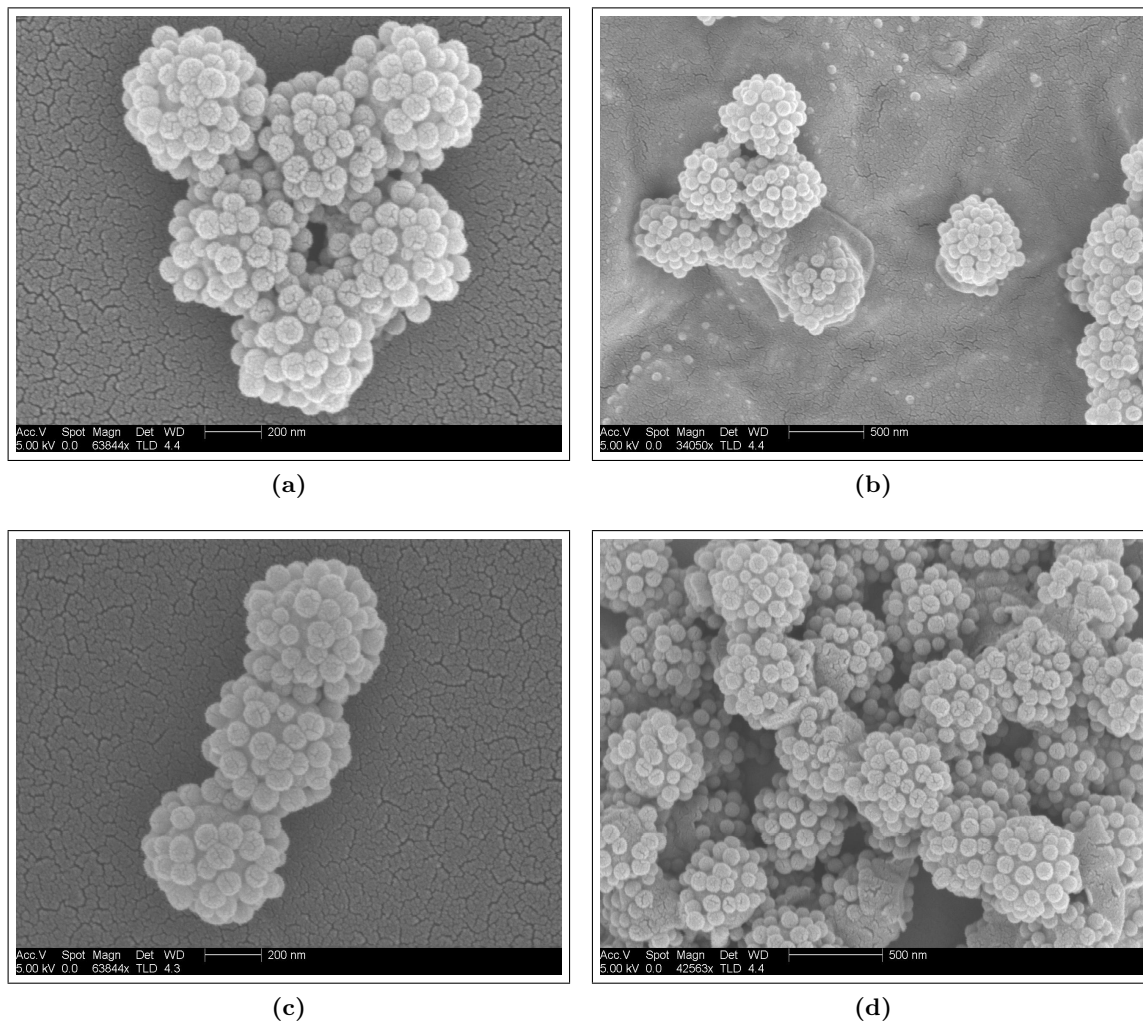
**Figure A.6:** TEM image of tube 5, with 0.01M NaCl after 0 hour mixing. Not all particles are adsorbed on the surface of the large particles.



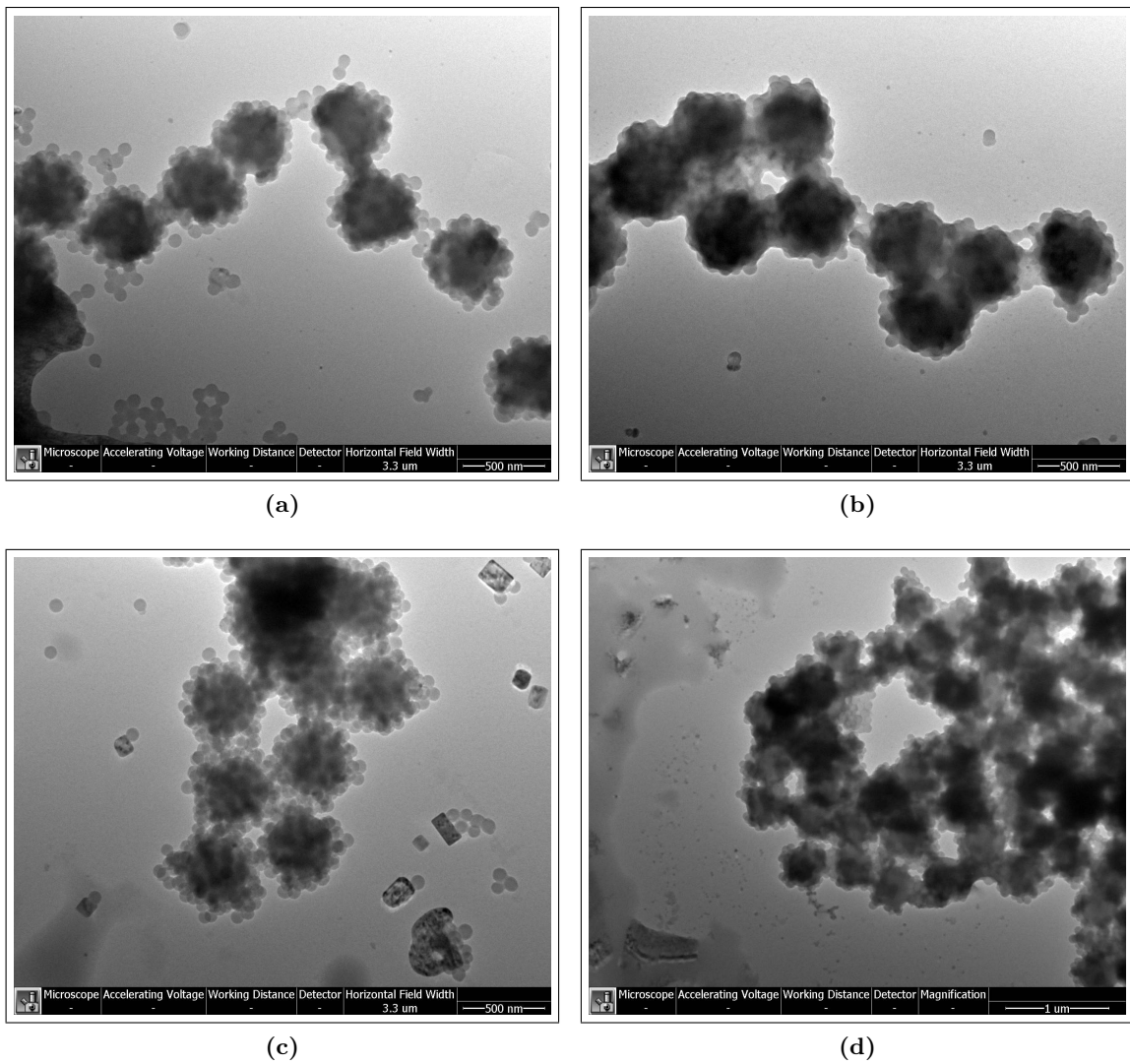
**Figure A.7:** TEM image of tube 5, with 0.01M NaCl after 24 hours mixing. There are more small particles adsorbed on the surface of the large particles.



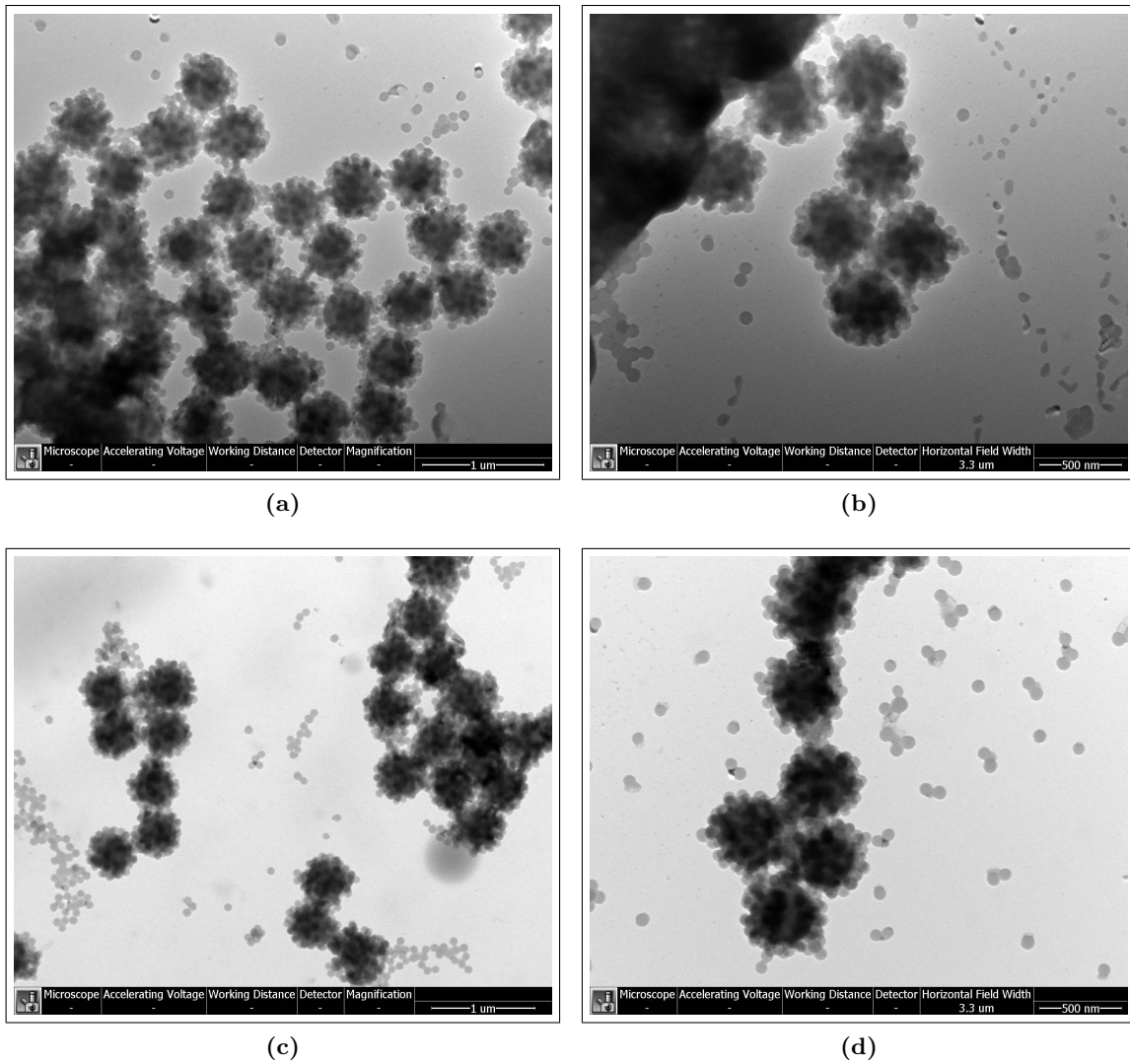
**Figure A.8:** TEM image of tube 5, with 0.01M NaCl after 24 hours mixing (same as A.2). It is hard to say that the coverage is better than fig 6.7. At least there can be said that after there are less "free" particles after 24 hours of mixing.



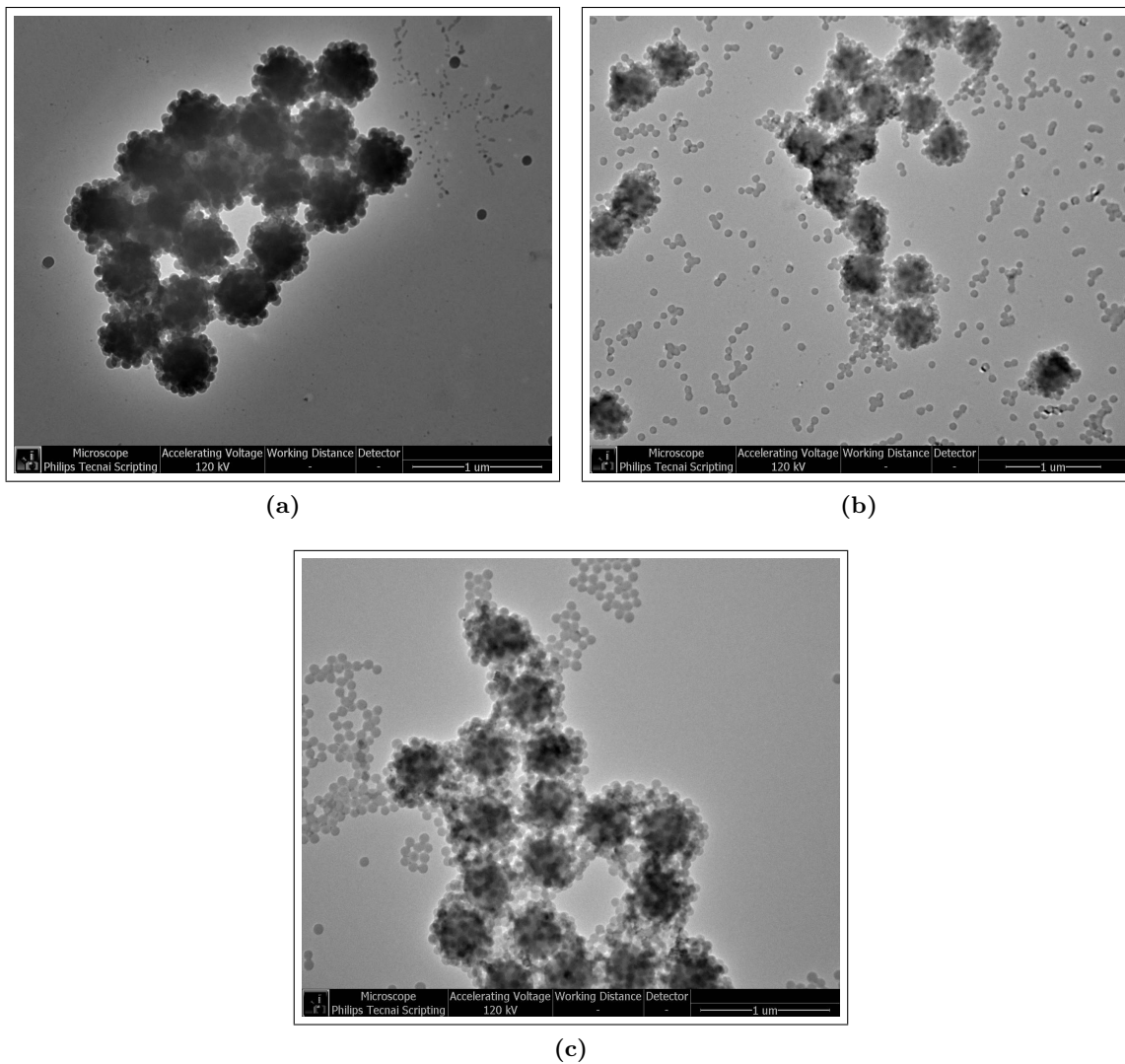
**Figure A.9:** Image (a) shows raspberry-like particles with 0.1M NaCl (Tube 4) that are water diluted. Image (b) shows raspberry-like particles with 0.1M NaCl (tube 4) that are diluted with 0.1M NaCl. The difference are a bit hard to see, but image (a) contains more bare spots. Image (c) and (d) are less covered than (a) and (b). Image (c) shows a picture of raspberry-like particles with 0.01M NaCl (Tube 5) that are water diluted. Image (d) shows raspberry-like particles with 0.01M NaCl (Tube 5) that are diluted with 0.01M NaCl. Here it is more easily to see that the coverage of image (c) is less than image (d). Furthermore, the particles are better distributed on figure (d).



**Figure A.10:** These are TEM images of the 0.1M sample from table 4.12. Image (a) to (d) corresponds to the different addition order "A" to "D". The difference between (a) and (b) are difficult to see. However, (c) is less covered than (a) and (b). Image (d) shows cluster formation.



**Figure A.11:** These are TEM images of the 0.01M sample from table 4.12. Image (a) to (d) corresponds to the different addition order "A" to "D". The difference between the images is hard to see. However, image (c) has a remarkable number of free particles, which implies a lower coverage.



**Figure A.12:** These are TEM images of different redispersing methods (stability test). Image (a) is made after shaking gently. Image (b) is made after redispersing with the vortex. Image (c) is made after ultrasonication. From (a) to (c) the coverage decreases and the free (small) particles increase.

## Appendix B

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### Calculation for the coverage percentage

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Using the solid content from the negatively charged polystyrene dispersion, the weight of "only the small particles (SP)" was calculated:  $SP(g) = DispersionWeight(g) * SC_s$ . When the weight of a single small particle ( $Q$ ) is known, the total amount of small particles (TSP) can be calculated:  $TSP = \frac{SP(g)}{Q(g)}$ . " $Q(g)$ " was calculated by multiplying the density of polystyrene with the volume of one particle:  $Q(g) = \frac{4}{3} * \pi * r_s^3(cm) * \rho_{polystyrene}(g/mL)$ .

With the same calculations, the total number of seed particles was calculated ( $TS_{eed}P$ ). Assuming that the raspberry-like particles have a spherical form (and contains only the monomer styrene), it follows that the density is the same of both the particles. This means that the volume percentage is proportional to the mass percentage and the number of free particles (FP) can be calculated with:  $FP = \frac{TAP(g) * V\%_s}{Q(g)}$ . Therefore, the total number of small particles on the surface of the seed particles (SPOSP) is also known:  $SPOSP = TSP - FP$ .

When the number of SPOSP is divided by  $TS_{eed}P$ , the number of small particles on one seed particle is known:  $\frac{SPOSP}{TS_{eed}P}$ . This number equals  $N$  from Equation 2.3.1. Finally, the coverage of the seed particles was calculated with this equation.