Chapter 5

Film formation of PMMA and PBMA latex particle (mono)layers studied by AFM

Abstract

This chapter focuses on the film formation of HDP monolayers of PMMA and PBMA latex particles, as well as thicker layers and mixtures of both samples, studied by Atomic Force Microscopy (AFM). It was found that the surface roughness, i.e. the height difference between the top of a latex particle and the intersect of two adjacent particles, could be determined very well and gave a good measurement of the particle deformation during annealing. A high molecular weight (MW) PMMA sample was found to deform much slower than a low MW sample, while monolayers, double layers and multilayers of the latter all deformed at an equal rate. Furthermore, the particle deformation was seen to obey to the visco-elastic time-temperature superposition principle. A major difference that was found between the PMMA and the PBMA latex samples was that cracks started to appear in the HDP monolayers of the former but not of the latter. These cracks were formed because the PMMA latex particles had shrunken upon annealing above \( T_g \). The difference was explained by the different hydrophilicities of the two polymers, which causes the PMMA particles to get swollen by water during the emulsion polymerization reaction, while the PBMA particles do not. Lastly, it was found that the deformation rate of PMMA particles increases with increasing PBMA latex particle content. The PBMA particles will appear to be empty voids in the close packed monolayer at high annealing temperatures, which results in less sterical hindrance for the PMMA particles. With no physical barrier at the PBMA particle side, the adjacent PMMA latex particles experience a higher chain mobility and thereby a higher particle deformation rate is measured.
5.1 Introduction

As is already discussed in the general introduction in Chapter 1, several techniques, such as freeze fracture TEM, have been used to elucidate the final shape of latex particles after film formation. It was found that the spherical particles deform into rhombic dodecahedra, thereby filling up the voids that were located between adjacent particles. Although these techniques give clear and undeniable evidence for the final particle structure, their disadvantage is that the sample becomes irreversibly damaged and can not be used any further.

A better way to study the particle deformation actually during the film formation process is by Atomic Force Microscopy (AFM), which is especially in tapping mode a nondestructive technique which does not need any pretreatment of the sample. The sample can undergo the same cycle of annealing at elevated temperatures for a certain time, cooling down and examination many times without any problems ¹.

Simply said, the functioning of the AFM can be compared to that of a gramophone needle when it tracks an LP. The heart of the AFM apparatus is formed by a sharp tip (analogous to the needle) which is attached to a bendable cantilever, as shown in Figure 5.1.

![Figure 5.1 Schematic representation of the AFM apparatus, with the tip (dark grey), cantilever (light grey) and reflected laser beam (dashed line) (0.55, 0.78)](image_url)

When a sample is being examined, the tip follows the contours of the sample surface, thereby maintaining a constant distance from the sample through all surface irregularities (which are analogues to the traces in the LP). Meanwhile, the cantilever has to bend up and down when the tip follows the contours of the sample surface. This deflection of the cantilever is being measured continuously and very precisely with a laser beam reflecting from its
topside. As can be seen in Figure 5.1, bending of the cantilever causes the laser beam to reflect in a slightly different direction due to the different angle of incidence at the top side of the cantilever. A split photodiode detector can distinguish these small deviations of the reflected beam, after which the computer program provides a clear height topography image of the scanned sample, which can even be displayed in 3D.

Of course, when doing these sorts of measurements, one still has to bear in mind that the AFM technique is literally a superficial technique, meaning that only the top surface of the sample is scanned and examined, regardless of the rest of the sample located below. However, the ability to scan the surface topography of a sample is also one of the major advantages of the AFM technique. It can provide quantitative data on the particle deformation during film formation due to the direct measurement of the so-called peak-to-valley distance, also known as the corrugation height or surface roughness, i.e. the height difference between the top of a deforming particle and the intersect of this particle with its neighboring particles \(^3,^2\). This distance is expected to decrease continuously during film formation and will eventually become zero, when the whole layer of latex particles has formed a uniform film.

5.2 Experimental

5.2.1 Latex synthesis

For the experiments that were performed to study the film formation of a monolayer of PMMA latex particles, the same latices were used as described in Chapter 2. In addition, a latex sample comparable in particle size and charge (\(\phi = 410\) nm and \(\zeta = -52.7\) mV, respectively) but with lower average molecular weight of the polymer binder was synthesized. This synthesis was done by a small alteration of the procedure described in Chapter 2, namely by the addition of 1.1 g of 1-dodecanethiol (Janssen Chimica, 98%, used as received) to the monomer before this latter was added to the water in the reaction flask.
5.2.2 Langmuir-Blodgett experiments

All LB experiments in this Chapter were performed in the same way as was done in Chapter 2, where the full procedures can be found.

5.2.3 Atomic Force Microscopy

Atomic Force Microscopy (AFM) measurements were performed on a Digital Instruments NanoScope IIIa in tapping mode, using Veeco Nanoprobe TappingMode Etched Silicon Probe (TESP) tips. All measurements were performed under ambient conditions.

5.2.3 Further analysis techniques

*Gel Permeation Chromatography*

The molecular weight of the polymer samples was determined by Gel Permeation Chromatography (GPC) using a Spectra Physics AS 1000 system with a Polymer Labs mixed-C column, a Viscotek H502 viscometer and a Shodex RI-71 differential refractive index detector. Measurements were performed at 30 °C with THF (Acros Organics, 99%, used as received) as eluens. THF was also used to make a solution of the dried polymer of approximately 1 mg/ml, which was filtrated using a 0.45 µm membrane before measurement to remove undissolved solids. Calculations were performed using the universal calibration method in the TriSec 3.0 program (Viscotek).

*Thermal Gravimetric Analysis*

The polymers thermal stability during annealing was determined by Thermal Gravimetric Analysis (TGA) on a Perkin & Elmer TGA 7. A sample of approximately 5 mg of the dried polymer was heated in a temperature scan from 25 to 550 °C with a rate of 10 °C/min while a microbalance continuously monitored the weight decrease of the sample. During another experiment the sample was kept at 150 °C and this time the weight decrease was monitored as a function of time.
**Differential Scanning Calorimetry**

The polymers glass transition temperature ($T_g$) was determined using Differential Scanning Calorimetry (DSC) on a Perkin & Elmer DSC 7. A sample of the latex dispersion was thoroughly dried under vacuum, after which approximately 5-10 mg of the dried polymer was placed in a aluminum DSC cup and heated from 0 to 150 °C at a rate of 10 °C/min. The $T_g$ of the polymer was calculated at the inflection point of the graph.

5.3 Results & Discussion

5.3.1 High molecular weight PMMA annealed at 150 °C

As was shown in the previous Chapters, the Langmuir-Blodgett method has proven to be a useful tool to obtain hexagonal dense packed (HDP) monolayers of latex particles. These HDP monolayers on solid substrates were now used to study the film formation by Atomic Force Microscopy (AFM), which is a very powerful method to investigate the changes in topography of such layers. The monolayers obtained in Chapter 2 were now annealed at a temperature of 150 °C, roughly 30 ° above the glass transition temperature $T_g = 117$ °C, to ensure enough mobility of the polymer chains and be able to see any structural changes at all. AFM scans were performed on the sample at various moments during annealing, which are shown in Figure 5.1 with a height topography image seen directly from above on the left and a 3D image on the right.
Figure 5.1 AFM images of high MW PMMA latex particle monolayer annealed at 150 °C; Top-view (left) and surface image (right)
This series of images shows two distinct features, namely the formation of cracks in the 2D colloidal crystal and the fading of the colloidal structure due to particle deformation. These features will now be discussed individually.

**Crack formation**

Probably the best noticeable effects that can be seen in these images is the formation of cracks in the 2D colloidal crystal, already after the short annealing time of 10 minutes. These cracks remain in the sample and can be seen throughout the whole annealing cycle from now on. A cross-sectional height profile of a latex particle monolayer before annealing and after the cracks have appeared is displayed below in Figure 5.2.

![Section Analysis](image)

*Figure 5.2 Cross-sectional height profile of high MW PMMA latex particle monolayer before annealing (top) and after 10 minutes of annealing at 150 °C (bottom)*
The top image shows that the latex particles in the close packed monolayer are almost perfectly aligned, with the tops of the particles at equal heights and with equal separation distances. The other image shows the drastic disruption of this close packed structure by the appearance of the deep cracks and subsequent formation of islands of particles.

Although the appearance of holes after annealing of a layer of latex particles with a surface without defects has been reported before, the explanation was then that particle-sized voids within the layer interior would be filled up by particles sinking in from the surface \(^1\). Because monolayers of latex particles are the subject of this study and thus it can be no matter of particles sinking down from higher layers, this explanation does not hold in this case.

Furthermore, in the first scan in which the cracks have appeared, the latex particles are still spherical in shape but their diameter has decreased by approximately 3\%. So it seems that the cracks are formed because the particles that were covering the substrate shrink completely during annealing. This shrinkage only occurs at temperatures above \(T_g\) as can be seen in AFM images from a sample of the same monolayer that was annealed at \(T = \) 55 °C and under vacuum to exclude any possible effect of water, as shown in Figure 5.3.

![AFM images from high MW PMMA latex particle monolayer annealed for 90 minutes at 55 °C under vacuum; top-view (left) and surface image (right)](image)

Comparison of these two images with the previous series proves that the cracks do not start to appear as the result of further drying, i.e. water loss of the sample, if in fact any residual water would still be present in the sample. In fact, it seems none of the processes seen
in Figure 5.1 have taken place in this case, as the particles in the monolayer have not deformed as well. The fact that annealing for this period of time does not seem to have any effect on the packing and the morphology of the latex particles is prove that these processes only occur at temperatures higher than the \( T_g \) of the polymer binder, as was also observed by others \(^8\).

To be certain that the shrinkage of the latex particles and thus the formation of the cracks in the monolayer are also not caused by degradation of the polymer and thereby loss of material at this elevated temperature, a Thermal Gravimetric Analysis (TGA) temperature scan was performed which is shown in Figure 5.4.

![Figure 5.4 TGA temperature scan of high MW PMMA](image)

This scan displays the regular TGA curve that has been found earlier for PMMA by other researchers as well \(^{11,10,3,9}\). Starting at room temperature, the sample remains thermally stable over a long temperature range. Only at a temperature of approximately \( T = 170 \, ^\circ\text{C} \) does the sample start to loose some weight, which is assigned to thermal scissions of head-to-head linkages. A slightly larger weight loss is found starting at \( T = 280 \, ^\circ\text{C} \), which is caused by scissions initiated at vinylidene chain-ends. At last, the main mode of degradation is that of random chain scission, which starts at \( T = 350 \, ^\circ\text{C} \) \(^{10,3}\).
Although this temperature scan proved that the polymer did not show any degradation at 150 °C, a second experiment was performed in which the sample was maintained at 150 °C and the weight loss was monitored as a function of time. However, after two hours, which is much longer than it took the cracks to appear in the monolayer, no weight loss was recorded at all. These TGA results combined are enough prove to state that the shrinkage of the latex particles is not caused by any degradation of the polymer binder.

With all other possible explanations eliminated, the most obvious reason for the particle shrinkage is some sort of stress relaxation accompanied by a change in particle density. The origin of this proposed phenomenon has to be searched in the emulsion polymerization mechanism. As described in almost every textbook 12,13, during the polymerization reaction the latex consists of small polymer particles swollen by monomer, as long as the degree of polymerization has not yet reached 100%, and possibly some water, depending on the hydrophilicity of the monomer and polymer in question. The glass transition temperature of these swollen particles will increase with increasing degree of conversion and will eventually rise above the polymerization temperature, at which point the polymerization reaction comes to an almost complete stop. From that moment on, the inner skeleton of the latex particles will be formed by stiff polymer chains which will maintain their structural orientation even when the residual monomer is extracted from the particle interior.

However, the simple fact that there used to be monomer inside the particle, swelling the polymer which would by now be the main component of the particle, causes the polymer density inside the particle to be less than that of the bulk polymer. Only when the temperature is raised above the polymers \( T_g \) will the mobility of the polymer chains become high enough so that this tenuous latex particle can collapse and the bulk density restored.

Gravimetric analysis of the final latex after completion of the polymerization reaction and subsequent comparison with the weighed in amounts of the various components revealed that the degree of conversion of this reaction was approximately 95%. The remaining, unreacted part of the monomer was very likely to be swelling the latex particles during the polymerization reaction and thus causing the particle interior to be less dense than would be expected, as stated above. This effect would even be strengthened by the difference in density between the monomer and the polymer. The density of PMMA is higher than that of MMA,
again resulting in a less dense particle interior when the average $T_g$ of the particle exceeds the polymerization temperature and the chain mobility gets frozen in.

However, as the observed shrinkage of the PMMA latex particles is far too high to be caused by these two factors alone, it is most likely that these latex particles are further swollen by water during the emulsion polymerization reaction. The water may have entered the polymer particle due to the relatively hydrophilic character of PMMA, which can especially be seen well when a comparison is made with PBMA latex particles. As will be seen later in this chapter, PBMA latex samples which are prepared by the same polymerization procedure do not display any shrinkage of the particles, and as both the polymer and the monomer are far less hydrophilic than (P)MMA, these particles are less likely to be swollen by intruding water.

Because the latex particles have only shrunken but have not deformed yet after 10 minutes annealing time, the measured decrease of the particle’s diameter can be used to calculate the decrease in volume as well, which turned out to be approximately 20%. Assuming that the PMMA particles have gained the bulk density of 1.2 g/cm$^3$ after these 10 minutes, the density inside the particles would be 0.96 g/cm$^3$ before annealing.

Particle deformation

The second feature that is visible in the annealing series is the deformation of the PMMA latex particles, which manifests itself by the fading of the spherical structure at the top of the monolayer. Fortunately, the appearance of the cracks, as discussed in the previous section, has lead to the situation that relatively large islands of particles are formed, in which the particles are still lying next to each other. This configuration allows the determination of the surface roughness, sometimes referred to as the peak-to-valley distance $^{14}$ or corrugation height $^{15}$, by which the height difference between the tops of the particles and the intersection point between two adjacent particles is meant. During annealing, this surface roughness is continuously decreasing, as is made more clear by the scheme presented in Figure 5.5.
The spherical particles possess a large total surface area as a result of the strong curvature of each individual particle. Given the chance during annealing above its T_g, the particles will deform in an attempt to lower this total surface area. This deformation proceeds by the means of mass flow in the direction indicated by the arrows in Figure 5.5. The progress of this particle deformation in time is shown in Figure 5.6.
The graph presented here displays an exponential decay in surface roughness, which takes a long time to eventually reach the value of zero. Other researchers have observed decay of surface roughness of this shape before 14, 16, 8.

As is just visible in the annealing series in Figure 5.1, after an annealing time of 900 minutes, or 15 hours, the individual latex particles can still be identified as the colloidal structure has not yet disappeared. Consequently, the surface roughness after 900 minutes is still at a value of approximately 1 nm, and only after 2700 minutes, or 45 hours, has the surface roughness completely decreased to zero. These results imply that this PMMA latex particle monolayer needs almost two days to form a film with a smooth surface, not taking the cracks into account. These cracks have not disappeared even after two days of annealing, which points out to very slow wetting of the substrate by the polymer binder. Surprisingly, and as of yet unexplainably, the type of substrate did not have any effect on either the crack formation, the particle deformation and the subsequent wetting by the polymer, as the behavior of this monolayer was identical on both hydrophilic glass and hydrophobic gold substrates.
As shown by Park et al., the surface roughness results can also be used to calculate the Brownian diffusion coefficient $D$, which relates to the effective particle radius $R_{\text{eff}}$ by Equation 5.1 \(^2, 8\).

$$R_{\text{eff}} = \frac{1}{2} \left( \frac{R^2}{\Delta z} + \Delta z \right) = \sqrt{6Dt} \quad (5.1)$$

in which $R$ is the average particle radius, $\Delta z$ the surface roughness and $t$ the annealing time. As depicted in Figure 5.4, the curvature of the latex particles decreases upon annealing, which makes it appear as if the top of that deformed particle is part of a much larger and still perfectly spherical particle with radius $R_{\text{eff}}$. Equation 5.1 now shows that a plot of the square of this effective radius against time should produce a straight line with a slope corresponding to the diffusion coefficient. Unfortunately, in this series the particle radius $R$ could not be determined accurately at annealing times longer than 300 minutes, but plotting these data up till 300 minutes indeed produces a straight line, as presented in Figure 5.7.

Figure 5.7 Effective particle radius squared vs. time of high MW PMMA latex particles annealed at 150 °C
The slope of the fitted line in this Figure is $6D = 8.79 \times 10^5$ nm$^2$/s, which can be rewritten in more commonly used units as $D = 1.47 \times 10^{-9}$ cm$^2$/s. Although the decrease of the surface roughness occurs simultaneously with interparticle diffusion of the polymer chains, this value of the diffusion coefficient found here is dramatically higher than the diffusion coefficient in the bulk, which is found in literature to be of the order of $D = 10^{-15}$ cm$^2$/s. This large discrepancy can be explained by taking the surface effects into account.

Polymer chains near the surface of a film in general or of the latex particles in this specific case are less sterically hindered due to the absence of neighboring chains at the outside, which makes them more mobile than the constrained polymer chains in the sample interior. Furthermore, the reduction of the total surface area of the sample provides an additional driving force for increased polymer diffusion and thus a higher diffusion coefficient.

Although the diffusion of the polymer chains near the surface is faster than in the bulk, particle deformation as seen in the previous Figures still takes a considerable time. This long particle deformation time is most likely the result of the high molecular weight of this particular sample, namely $M_n = 134 \times 10^3$ g/mole and $M_w = 528 \times 10^3$ g/mole. This high MW drastically decreased the chain mobility of the polymer binder, thereby increasing the resistance to deformation of these particles and probably polymer interdiffusion as well, which makes it very time-consuming to study this phenomenon. Therefore, in order to achieve a monolayer displaying particle deformation, and thus film formation as a whole, on a shorter time-scale, similar experiments were performed with a PMMA latex sample with lower MW, as will be discussed in the next section.

### 5.3.2 Low molecular weight PMMA annealed at 150 °C

As discussed in the previous section, particle deformation and thus film formation as such, takes a very long time when a high MW PMMA sample is used, as a result of the decreased chain mobility of the polymer binder. The time-scale on which this study is performed can be drastically decreased when a sample of lower MW is used, which in this case is obtained by the addition of a chain transfer agent (CTA) to the reaction mixture during the emulsion polymerization.
As all other synthesis parameters were kept constant, the addition of a CTA resulted in a PMMA sample with similar particle size and very likely comparable surface charge, but with a MW of \( M_n = 49 \times 10^3 \text{ g/mole} \) and \( M_w = 129 \times 10^3 \text{ g/mole} \), indeed much lower than the sample used previously, as expected. Related to this lower MW was the lowering of the \( T_g \) of this sample, which was determined by DSC to be \( T_g = 105 \degree \text{C} \). That this lower MW, and thereby lower \( T_g \), has a dramatic effect on the rate of particle deformation in a monolayer is made clear by the annealing series presented in Figure 5.8, performed under similar conditions as the high MW latex particle monolayer.
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$t = 0 \text{ min}$

$t = 10 \text{ min}$

$t = 30 \text{ min}$
Although not the best of images, the double layer at $t = 0$ min shows that the second layer also has a large tendency to form a 2D colloidal crystal on top of the first one. The packing of the particles is slightly less ordered however, probably due to the apparently increased roughness of the substrate, which is now formed by the first latex particle monolayer instead of a smooth glass slide.

Upon annealing, the double layer displays cracks in the particle arrays just as the monolayer did, but now the cracks seem to be less regular. Where almost all the cracks in the monolayer were straight and along the direction of the three axes of the 2D crystal, the cracks in the double layer are irregular in shape and direction. No clear explanation can be given for this difference, but it could be caused by the fact that all particles in both layers are shrinking, but the resulting clusters of particles are not formed at the same positions in both layers. Particles in the second layer could then end up above cracks in the first layer and, as a result of that, would then probably fall down into that first layer. This mechanism would yield a pattern in the cracks that could actually be regarded as some sort of superposition of two individual crack patterns, one for each layer.

A thick multilayer of latex particles was obtained by the drying of a droplet of the base latex on a glass substrate, which results in a 3D colloidal crystal as shown in Figure 5.12.
Figure 5.8 AFM images of low MW PMMA latex particle monolayer annealed at 150 °C; Top-view (left) and surface image (right)
This series of images shows that the formation of cracks in the 2D colloidal crystal structure is not influenced by the MW of the polymer binder, as in this monolayer they are clearly present as well after 10 minutes annealing time. However, in contrast to the high MW sample, the cracks do fade away in this monolayer, as can be seen best in the last image representing a long annealing time of roughly 3 days. This image shows that wetting of the substrate by the polymer binder occurs, as the cracks tend to get filled up again by the polymer.

This relatively quick film formation of the low MW PMMA latex sample, as compared to the high MW sample, gave the opportunity to check the validity of the suggestion made earlier that the cracks in the HDP monolayer are the result of stress-relaxation in the latex particles. By scratching through the monolayer right to the substrate at various annealing times, the total film thickness of the sample could be determined by AFM as well. Before annealing, this thickness turned out to be 410 nm, as expected equal to the diameter of the latex particles. At an annealing time of 10 minutes, when the cracks in the monolayer have appeared but the latex particles are still spherical in shape, the thickness has decreased to a value of 375 nm. When the density inside these particles is set to the bulk density of PMMA, being 1.2 g/cm³, foaming up the particles to particles with equal mass but with the diameter seen at $t = 0$ yields a density of 0.96 g/cm³. Theoretically, when a HDP monolayer of these low-density latex particles has formed a uniform film in which the particles are completely deformed and all voids are filled up, the thickness of that film is calculated to be 220 nm. This thickness is indeed what is measured on average after a long annealing time of several days, which confirms that the assumption towards the decreased particle density before annealing is correct.

Furthermore, a second observation that can be made from the annealing series is that the time it takes the particles to deform and lose their identity is much shorter than was the case for the high MW sample. Again, this decrease in surface roughness is best shown when plotted in a graph against time as is done in Figure 5.9.
Figure 5.9 Surface roughness of low MW PMMA latex particle monolayer during annealing at 150 °C

The surface roughness of this low MW latex particle monolayer before annealing is only slightly lower than that of the high MW sample, and as both are HDP monolayers, this resemblance is an extra confirmation that the particle size of these two samples are almost identical. However, the main observation from Figure 5.9 has to be that the observed surface roughness is decreasing much faster than it did in the case of the high MW monolayer. The surface has already become completely smooth after the relatively short time of 90 minutes, again as seen on a particle scale and not taking the larger cracks into account. After that, the polymer ridges just start to get smoothed, filling up the cracks that are separating them, and eventually an almost completely smooth film will be formed.

Using Equation 5.1 in a similar way as was done in the previous section on high MW PMMA, a graph of the square of the effective particle radius versus annealing time can be drawn up which, as in the previous case, gives a straight line with a slope 6D. This graph is depicted below in Figure 5.10.
Figure 5.10 Effective particle radius squared vs. annealing time of low MW PMMA latex particles annealed at $T=150$ °C

The diffusion coefficient for low MW PMMA, as calculated from the slope of this graph, is $D = 2.09 \times 10^{-9}$ cm$^2$/s, roughly one and a half times the value of the high MW PMMA sample. This higher value for $D$ confirms the faster film formation as was already observed by comparing the decrease of the surface roughness in Figures 5.6 and 5.9.

The fact that the chain mobility of the low MW PMMA sample is increased so much over that of the high MW sample, and that therefore the particle deformation rate is increased likewise, gives rise to experimental time-scales that are easily handled and that allow easy and fast comparisons to other results, such as the film formation of a double layer or even a relatively thick multilayer of latex particles. These examples will both be discussed separately in the following sections, after which the effect of the annealing temperature on the film formation of this low MW PMMA latex particle monolayer will be investigated.
5.3.3 Low molecular weight PMMA double layer / multilayers annealed at 150 °C

In addition to the low MW PMMA particle monolayer, as described in the previous section, similar annealing experiments were also performed with a double layer of the same latex particles as well as a thick multilayer. The double layer was obtained by two successive depositions of a stabilized particle monolayer from the LB trough onto a glass substrate, of which the first monolayer was annealed for 10 seconds to ensure a firm connection of the latex particles to the substrate. The second monolayer was then deposited onto this first one by repeating the vertical dipping sequence with an identical but fresh monolayer. As the substrate is now different for the second monolayer due to the particles that are already adhered to the glass substrate, the layer morphology turned out to be slightly less ordered, as can be seen in Figure 5.11.
Figure 5.11 AFM images of low MW PMMA latex particle double layer annealed at 150 °C;
Top-view (left) and surface image (right)
Figure 5.12 AFM images of low MW PMMA latex particle multilayer annealed at 150 °C;
Top-view (left) and surface image (right)
Clearly visible in the first images are the edges of the particle layers that were not completely built up as there were not enough particles available anymore towards the end of the drying. Due to this particle starvation, this image reveals very nicely that the 3D colloidal crystal is made up of 2D crystals, or HDP monolayers, stacked on top of each other.

Annealing this thick multilayer of PMMA latex particles does not result in the formation of visible cracks anymore. Probably because there are now so many layers lying on top of each other, cracks of any layer will be covered by particle clusters from other layers, and so as a result a waving surface is observed with large valleys instead of relatively narrow cracks.

Despite these differences on the larger level of particle ordering, the particle deformation of both the particle double layer and the multilayer does not differ from that of the monolayer. All points of the annealing series of these three samples are roughly positioned on one single, exponentially decaying curve which is shown below in Figure 5.13.

![Figure 5.13 Surface roughness of low MW PMMA latex particle samples during annealing at 150 °C; monolayer (●), double layer (▲) and multilayer (■)](image-url)
After an annealing time of 90 minutes, all three samples no longer display any surface roughness, meaning that the latex particles have deformed to such an extent that the tops of the particles were not protruding from the surface anymore but formed a smooth surface instead. This similarity between the monolayer, double layer and multilayer suggests that it is of no importance for the deformation of the latex particles at the surface, i.e. for the diffusion coefficient of the polymer chains near the surface, how many layers of particles are lying underneath them. Whether this number is none, only one or simply many, the particles at the top will deform with the same rate, which shows that latex particle monolayers can be used especially as a model for the top layer of a waterborne coating in practice.

5.3.4 Low molecular weight PMMA annealed at 137 °C and 163 °C

The high MW PMMA sample was annealed at a temperature of 150 °C, which was chosen rather arbitrarily as a nice round number above $T_g$ of the polymer. For precise comparisons, the low MW PMMA sample was annealed at this same temperature. However, due to the lower MW of this sample, its $T_g$ was also lower and so annealing was performed at the same absolute temperature but not at the same temperature increase above $T_g$. The annealing temperature of the high MW sample was 33 ° above its $T_g$, so in order to make a more precise comparison between the high and the low MW PMMA latices, the low MW sample is also annealed at a temperature of $T=137$ °C. Scanning of the surface of the monolayer by AFM at various time intervals during annealing resulted in a similar annealing series as seen previously but now with a lower rate of particle deformation.

To make a small series of annealing temperatures, the same measurements were also performed at an annealing temperature that was 13 ° above the round number of $T=150$ °C, i.e. at $T=163$ °C. Again, a similar annealing series was the result, but now, not surprisingly, with particle deformation occurring at a higher rate.

Because the AFM images do not change from the sample annealed at $T=150$ °C apart from the moment in time that they are recorded, they will not be shown here for the annealing temperatures of $T=137$ °C and $T=163$ °C. In fact, the effect of the annealing temperature on the film formation can be made visible in the best way by plotting the surface roughness of the sample against annealing time at the various temperatures, as shown in Figure 5.14.
Figure 5.14 Surface roughness of low MW PMMA latex monolayer during annealing at T=137 °C (■), T=150 °C (●) and T=163 °C (▲); individual curves (left) and superimposed curves with factors 2.0 and 2.6 (right)

The left graph in Figure 5.14 shows that, as intuitively expected, the rate of film formation is higher at higher annealing temperatures. Where it takes the low MW PMMA particle monolayer approximately 90 minutes to lose its surface roughness on a particle scale at an annealing temperature of T=150 °C, it takes 300 minutes to achieve this result when the temperature is decreased to T=137 °C and only 35 minutes when it is increased to T=163 °C. In fact, these three individual curves as presented here display excellent time/temperature superposition, which is an indication for pure viscoelastic behavior of the particles. When the time-axis of the surface roughness curve at T=163 °C is multiplied by the superposition factor 2.0, the curve coincides almost perfectly with the surface roughness curve at T=150 °C, which in turn needs a superposition factor 2.6 to coincide with the curve at T=137 °C. Taking these superposition factors into account, all three series of data are merged into one single master curve, as shown in the left graph in Figure 5.14.

5.3.5 PBMA annealed at 80 °C

The main part of this current Chapter is focused on the film formation of HDP monolayers of PMMA latex particles, which were also topic of investigation in Chapter 2. However, as was previously seen in Chapter 3, PBMA latex particle monolayers behave slightly differently during LB experiments than PMMA latex particle monolayers. In order to
find out whether they also display different behavior during annealing experiments, a similar series of annealing and AFM measurements were performed for a PBMA latex particle monolayer with $M_n = 66 \times 10^3$ g/mole and $M_w = 203 \times 10^3$ g/mole in a similar way as was done before for a PMMA sample. The only difference in this case was of course the annealing temperature, the $T_g$ of PBMA being far lower than that of PMMA. At an annealing temperature of 80 °C, approximately 45 ° above $T_g$, the results shown in Figure 5.15 are obtained.

Figure 5.15 AFM images of PBMA latex particle monolayer annealed at 80 °C; Top-view (left) and surface image (right)
Because the added value of more images is only little due to their similarities to previous images, only two points of the annealing series are displayed here. At \( t = 0 \) minutes, before annealing, the PBMA latex particles form a HDP monolayer, as was already seen earlier in Chapter 3. The second pair of images, after an annealing time of 30 minutes, shows that the latex particles still form a close packed monolayer without any visible cracks, although the particles have already started to deform. Even after the longest annealing times, no cracks in the HDP monolayer were observed, which indicates that, in contrast to PMMA latex particles, PBMA latex particles already have a density matching the polymer’s bulk density before annealing. As already mentioned previously, this difference between the two polymers is most likely the result of their different hydrophilicities, which causes the PMMA latex particles to get swollen by water during the emulsion polymerization reaction and the PBMA latex particles not.

In a similar way to the PMMA samples before, the particle surface roughness of the PBMA latex particle monolayer was measured during the annealing series, which yielded the graph displayed below in Figure 5.16.

![Figure 5.16](image)

**Figure 5.16** Surface roughness of PBMA latex particle monolayer during annealing at 80 °C
Strikingly, in comparison to the surface roughness vs. annealing time graphs of the PMMA latex samples, this graph of the PBMA latex sample displays a very rapid decrease of the particle roughness in the first hour, followed by a rather slow further decrease until this surface roughness has completely decreased to zero after 900 minutes or 15 hours. The initial quick particle deformation rate is also made visible by the steep slope of a graph of the square of the effective particle radius as a function of annealing time, as depicted in Figure 5.17.

![Graph of PBMA latex particles annealed at 80 °C](image)

**Figure 5.17** Effective particle radius squared vs. time of PBMA latex particles annealed at 80 °C

Again, like in the previous cases, all these data points are forming a straight line, of which the slope $6D$ eventually results in a diffusion coefficient of $D = 1.33 \times 10^{-8}$ cm$^2$/s. This value is roughly a factor 10 higher than those found for the PMMA latex samples, which is probably caused by the fact that the annealing temperature for PBMA was set 45 ° above its $T_g$, while that difference was only 35 ° for PMMA. This extra temperature increase of 10 ° results in a higher chain mobility of the PBMA polymer chains, and thereby a higher particle deformation rate.

However, the deformation rate drops drastically after the first hour of annealing, and in the end it takes this PBMA sample just as long as the high MW PMMA sample to completely lose the particle identity and gain a surface roughness of zero, namely 15 hours. As of yet, it remains unclear why this dramatic decrease in deformation rate occurs, but it might be related
to the fact that these monolayers do not show any crack formation during annealing. Because the PBMA latex particles remain closely packed, even after long annealing times, all particles are always surrounded by other particles all around, where in the case of PMMA samples a lot of particles are next to the formed cracks. These cracks allow these specific PMMA particles a higher chain mobility due to surface effects at these particle-crack interfaces. In contrast to this, no PBMA particles have adjacent cracks but all are confined and thus more sterically hindered, which might result in a relatively low chain mobility that becomes especially apparent at longer annealing times. This effect might then even become dominant over the increased chain mobility due to the higher annealing temperature, thereby resulting in the observed sudden decrease in particle deformation rate. However, as no further research is performed to investigate these observations, this explanation remains purely speculative.

5.3.6 PMMA / PBMA latex mixtures annealed at 150 °C

As already described in Chapter 4, there are only few publications about mixtures of different latex particles, of which the majority are dealing with mixtures of relatively hard and soft particles and the subsequent film formation of those. One of the interesting results that were found, at least for the topic that is discussed in the current Chapter, was that the interdiffusion of the soft component was seriously hindered by the presence of the hard component. The observed diffusion hindrance of the soft component was explained by a so-called obstacle effect, meaning that the surface of the hard particles in the mixture are forming a physical barrier for the soft polymer chains. The effective outcome of this situation is that the soft polymer in the vicinity of the hard particles experiences reduced mobility as compared to the rest of the soft component, which is surrounded by similar material in a more bulk-like phase.

To investigate if a similar phenomenon can be observed in the particle deformation of a mixed monolayer of relatively hard and soft latex particles, annealing experiments and subsequent AFM measurements were performed on samples with varying PMMA/PBMA ratio, as were already discussed in Chapter 4. To study the effect of hard latex particles on the deformation of the soft latex particles and vice versa, annealing series were performed at both
70 °C and 150 °C, respectively. The latter will be discussed first in the current Section, the former in the following Section.

The resulting graphs of the deformation of PMMA latex particles in the presence of various amounts of soft PBMA latex particles as a function of the annealing time are depicted in Figure 5.18.

![Graph](image)

**Figure 5.18** Surface roughness of PMMA part of PMMA/PBMA mixed latex monolayers during annealing at $T=150$ °C; PMMA/PBMA ratios 1/0 (pure PMMA, ■), 10/1 (○), 2/1 (▲) and 1/1 (▼).

This Figure shows that the inclusion of 10% PBMA latex particles does not have a significant effect on the particle deformation of the PMMA latex part of the monolayer. The curves of the pure PMMA latex particle monolayer and that of the 10/1 ratio monolayer coincide to such an extent that no significant difference in the particle deformation rate can be observed.

However, if the PBMA content is increased more to a 2/1 or even a 1/1 ratio, the deformation rate of the PMMA latex particles increases strongly, as can be seen by the downward shift of the curves in Figure 5.18. Oppositely to the cases that were already investigated by Odrobina and Feng, but also due to their findings not unexpected, the presence of relatively soft latex particles seems to increase the particle deformation and
thereby probably the interdiffusion of hard latex samples. The most obvious explanation would now also be the opposite of that of the case of hard filler particles in a soft particle matrix, namely that those hard particles that are located in the vicinity of the relatively soft particles experience an increased mobility. In the case of hard filler particles in a matrix of soft particles, those hard particles act as a physical barrier, as explained earlier. In this opposite case, however, the soft particles in the matrix of hard particles act as a hole, an empty lattice site in the 2D colloidal crystal of the latex particle monolayer. It appears to the hard particles as if the soft particles are not even there, because they are far more mobile and flexible at the high annealing temperatures that are used to insure chain mobility in the hard latex particles. And with practically no particle next to them, the adjacent PMMA latex particles are less sterically hindered than in the case of a HDP monolayer of PMMA particles only, resulting in the observed increased deformation rate.

Unfortunately, due to time limitations, similar measurements for the PBMA part of the mixed particle monolayers at 80 °C were not performed. However, from the result found here and by Odrobina and Feng, and from the explanation for these results, it is expected that the behavior of the PBMA latex particles would be completely opposite to that of the PMMA latex particles. The relatively hard PMMA particles incorporated in the HDP PBMA latex particle monolayer would act as rigid obstacles, physical barriers that significantly hinder the PBMA chains in their mobility and thus decrease the particle deformation rate considerably.

5.4 Conclusion

This chapter is focused on the film formation of PMMA and PBMA latex particles studied by AFM. This technique is extremely suitable to study surface characteristics of the latex particle monolayers and can thus be used to monitor the particle deformation upon annealing.

It was found that it takes a high MW PMMA latex sample with a $T_g$ of 117 °C 15 hours of annealing at 150 °C to form a completely smooth surface on a particle scale, meaning that the peak-to-valley distance or corrugation height has decreased to zero. On a larger scale, however, the surface is not smooth at all due to the formation of cracks in the monolayer. These cracks already appear after an annealing time of 10 minutes, when the latex particles are
still spherical in shape but have shrunken to a smaller size. The explanation for this observation is that the particles before annealing do no yet have the bulk density of PMMA, but a lower density of 0.96 g/cm$^3$. This decreased density inside the particles is the result of swelling of these particles during the emulsion polymerization reaction, due to the relatively high hydrophilicity mostly by water. Upon annealing at a temperature higher than the polymer’s $T_g$, a sort of volume- or stress-relaxation can occur in which the polymer chains collapse onto each other and the particles shrink.

A low MW PMMA sample was found to deform much faster. Because the $T_g$ of this sample was much lower, namely 105 °C, its chain mobility and thus the particle deformation rate was much higher at the same annealing temperature. This sample too only 90 minutes to form a completely smooth film on a particle scale. The diffusion coefficient of the polymer chains was calculated to be higher than that of the high MW sample as well. Furthermore, due to this high deformation rate, annealing for a long time of several days yielded a uniform film that was almost completely smooth overall. The thickness of this film was in good agreement with what was expected from a HDP monolayer of latex particles with the decreased density as calculated earlier.

Double layers and relatively thick multilayers of the low MW PMMA latex sample displayed a similar particle deformation rate as the monolayer. Because the AFM technique only allows the topside of the sample to be measured, these results imply that deformation of the top layer of latex particles occurs independently from the total number of layers. Despite the amount of material underneath, the latex particles directly at the surface will deform with the same rate.

The low MW PMMA latex sample was also annealed at both a lower and a higher temperature, and not surprisingly, the particle deformation rate consequently decreased and increased, respectively. Better yet, the particle deformation displayed a very nice time-temperature superposition, which was demonstrated by the fact that all three surface roughness vs. annealing time graphs could be superimposed into one curve by multiplying the original curves with a superposition factor.

PBMA latex particles monolayers were found to behave a bit different from the PMMA samples. During annealing, these PBMA samples did not display any cracks being formed in the HDP monolayer. Because these particles were not swollen during the emulsion
polymerization reaction, owing to the highly hydrophobic character of the polymer, they do not have a lower density than the bulk material and thus do not shrink upon annealing. Furthermore, it was found that, despite an initial rapid particle deformation due to a relatively high annealing temperature, it takes the PBMA latex particle monolayer also along total annealing time of 15 hours to reach a surface roughness of zero. A possible explanation for this phenomenon, which seems rather contradictory, might be that the lack of cracks in the monolayer forms a sterical hindrance for the chain mobility.

Finally, the mixed particle monolayers of Chapter 4 were investigated, and it was found that the particle deformation rate of the PMMA latex particles at an annealing temperature of 150 °C increased with increasing PBMA latex content. These results were in agreement with results reported in literature, and can be explained by sterical hindrance once more. At these high annealing temperatures, the PBMA latex particles deform very rapidly and will display a considerable amount of flow. From the point of view of the harder PMMA latex particles, the lattice sites occupied by the PBMA particles appear to be empty voids in the regularly packed monolayer, giving adjacent PMMA particles more freedom to move, i.e. a higher chain mobility.

References