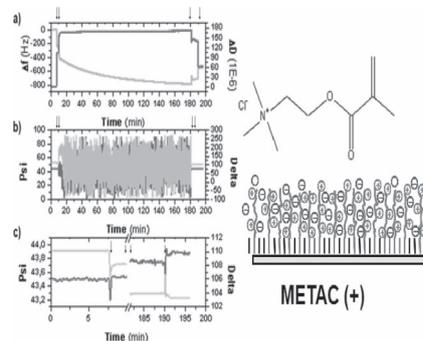


Effect of the Density of ATRP Thiol Initiators in the Yield and Water Content of Grafted-From PMETAC Brushes. A Study by Means of QCM-D and Spectroscopic Ellipsometry Combined in a Single Device

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Poly {[2-(methacryloyloxy)ethyl] trimethylammonium chloride} (PMETAC) brushes are synthesized by atom transfer radical polymerization from mixed monolayers of ω -mercaptoundecyl bromoisobutyrate thiol (initiator) and 1-undecanethiol (blank). Initiator density is varied from 100% to 1% by the molar ratio of initiator to blank in solution. Brush growth is followed in situ by a single device combination of a quartz crystal microbalance with dissipation (QCM-D) and spectroscopic ellipsometry. Acoustic mass (m_{acous}) and optical mass (m_{opt}) are simultaneously recorded. Brush hydration is calculated from the difference between m_{acous} and m_{opt} . The percentage of water lost during brush collapse in NaCl solution at concentration from 10^{-3} M to 1 M is quantified for each initiator density.



1. Introduction

Polyelectrolyte brushes are monolayers of polyelectrolyte molecules tethered by one end of the polymer chain to a surface, whereas the other end of the chain remains free and exposed to the environment.^[1–5] The polymer chains of a brush display conformational changes with the ionic strength,^[6,7] which result in height variations and changes in the packing density of the brush. This property has inspired the use of polyelectrolyte brushes as “smart” surfaces or nanoactuators.^[8–10]

It has been shown that the quartz crystal microbalance with dissipation (QCM-D) monitoring is a powerful technique to follow the growth of poly {[2-(methacryloyloxy)ethyl] trimethylammonium chloride} (PMETAC) polyelectrolyte brushes and to characterize their response with the ionic strength.^[11] The QCM-D response, that is, the resonance frequency f and the energy dissipation D of the shear oscillatory motion of a piezoelectric quartz crystal sensor, is highly sensitive upon adsorption or desorption of materials and also to changes in the mechanical properties of a deposited material.^[12,13] Mass resolution is on the order of a few ng cm^{-2} . Owing to its acousto-mechanical transducer principle, the QCM-D technique is not only sensitive to the adsorbed molecules but also to the solvent retained within or hydrodynamically coupled to the surface-bound film. Therefore, from the QCM frequency response alone, it is difficult to discriminate between the adsorbed polymer mass and the contribution of the solvent coupled to the polymer. Polyelectrolytes are charged molecules with hydrated monomers. Besides that, water

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can be entrapped either in cavities between neighboring chains, as reported by some authors.^[14,15] The QCM-D will thus sense the total mass of brush, consisting on polyelectrolyte and water. On the contrary, it can measure the amount of water that is reversibly lost during collapse with the ionic strength.^[16]

Spectroscopic ellipsometry is an optical technique, wherein the change in the polarization state of an incident light wave upon reflection at an interface is measured. Variations in the ellipsometric angles ψ and Δ as a function of the wavelength λ are detected with high accuracy. These are connected with changes in the polarization of light. Proper data treatment of the simultaneous *in situ* determination of ψ and Δ provide quantitative information on the refractive index, thickness, and mass of a growing film.^[17,18] As ellipsometry is sensitive to differences in the optical density between adsorbate and bulk solution, it essentially senses the adsorbate mass. Therefore, the comparison of the mass values measured by both QCM-D, wet mass and ellipsometry, dry mass allows for the calculation of the water content of a polyelectrolyte brush. The main advantage brought by this combination of ellipsometry and QCM-D in a single device is that the responses of both techniques are measured in parallel and in real time from the same sample under identical experimental conditions.^[19]

In previous papers, we have shown the application of combination of both techniques to study the water content of polyelectrolyte multilayers and hydrated brushes. For multilayers, we have shown that the combination of two techniques allows to determine the changes in water content after each layer deposition and how this is affected by the procedure employed for the assembly.^[19] For hydrated brushes, we have been able to determine the water content of PMETAC, poly (potassium 3-sulfopropyl methacrylate) (PSPM), and poly (*N*-isopropyl acrylamide) brushes (PNIPAM).^[20] From the water content, we have been able to determine the percentage of water lost during the collapse either with the ionic strength for PMETAC and PSPM or with the temperature for PNIPAM.^[20]

In this article, we present the combination of spectroscopic ellipsometry and QCM-D in a single device to study the growth and water content of PMETAC brushes assembled on gold surfaces, when the polyelectrolyte chains are grafted from mixed monolayers of initiator/non-initiator thiol-mixed solutions. Besides the ease of assembly, the synthesis of a brush from a monolayer of thiol initiator molecules has the advantage that the density of initiator can be varied by incorporating a non-initiating thiol in the solution from which the thiol monolayer is formed. The change in density of initiator will impact in the growth and nature of the chains forming the brush. Decreasing the density of initiators will reduce the number of polymer chains but, at the same time, the formed chains

will have more lateral space to grow. The length of the chains and the space between chains will directly influence the water content of the brush. The longer the chains the more water will be associated with the chains. On the contrary, the higher the density of chains in the brush the less water will be entrapped between the polyelectrolyte chains forming the brush.

To vary initiator density, we used mixed solution of initiator, ω -mercaptoundecyl bromoisobutyrate thiol, and a blank thiol, 1-undecanethiol, as previously described by Jones et al.^[21] The actual initiator concentration in the monolayer may not be that of the solution, taking into account the differences in size of the thiols and the probably different kinetics of assembly of the two thiols employed. Despite that, the method works effectively to vary the initiator concentration. We will always refer in text to the thiol monolayers with the concentration of initiators used in the coating solution.

The combination of QCM-D and ellipsometry will provide the quantification of the mass of polymer synthesized and the water associated with this mass. In this way, we can decouple the actual mass of the polymer from the water retained in the brush and obtain the actual yield of the polymerization as a function of the number of initiating molecules. Although it is not possible to measure by this means the length of the individual polymer chains for the different initiator densities nor the space between the chains, the quantification of both polymer and water content will provide a better characterization of the properties of the brush as the density of initiators is varied.

Also, knowing the amount of water in the brush will make possible to quantify the percentage of water lost during the collapse for the different initiator densities. The amount of water lost during collapse is highly related to the packing of the brush and the presence of water entrapped between the chains. We will see that the water lost is not maximal at the highest density of initiators. Also, by reducing the amount of initiator down to just 1% is not resulting in the loss of water from the brush, hinting that the polyelectrolyte chains are extended on the surface, not forming a brush-like structure anymore.

2. Experimental Section

2.1. Materials

{[2-(Methacryloyloxy)ethyl] trimethylammonium chloride} (METAC, $\bar{M}_w = 207.5 \text{ g mol}^{-1}$), 80% in water, dimethylformamide 99.85% (DMF), copper (I) chloride, 2,2'-bipyridyl, and 1-undecanethiol 98% were purchased from Aldrich and were employed without further purification. The ω -mercaptoundecyl bromoisobutyrate initiator thiol was synthesized as described in the literature.^[21] Sodium chloride and lithium perchlorate salts were purchased from Fluka. Ethanol (96%) was purchased from

Scharlau S.A. Water was purified using a nanopure purification system (Thermo Scientific Barnstead).

2.2. In situ Combination of QCM-D and Ellipsometry

The growth of the polymer brushes was followed simultaneously, by QCM-D and ellipsometry, from the same surface and in liquid environment. Measurements were performed using a purpose-designed flow cell (Q-Sense AB, Västra Frölunda, Sweden) with a total volume of $\approx 300 \mu\text{L}$. The flow cell was attached to a Q-Sense E1 setup, providing access to QCM-D data, and mounted on a spectroscopic rotating compensator ellipsometer (M2000V, Woollam, NE, USA), providing access to ellipsometric data. QCM-D data, Δf and ΔD , were acquired at six overtones ($i = 3, 5 \dots 13$, corresponding to resonance frequencies of $f_i \approx 15, 25 \dots 65 \text{ MHz}$) simultaneously, with sub-second time resolution. Ellipsometric data, Δ and Ψ , were acquired over a wavelength range from $\lambda = 380$ to 1000 nm , simultaneously, at 65° angle of incidence, and with a time resolution of $\approx 5 \text{ s}$. The working temperature was 23°C .

2.3. Assembly of Thiol Monolayer

PMETAC brushes were synthesized from a monolayer of thiols formed from solutions of ω -mercaptoundecyl bromo isobutyrate (thiol initiator) and 1-undecanethiol 98% (blank thiol) in different ratios. The monolayer was assembled on gold-coated quartz sensors (QSX 301, 4.95 MHz, Q-Sense AB). The sensors were pre-treated with UV/ozone (BioForce Nanosciences, Ames, IA, USA) for 30 min and then exposed overnight to the thiol solution in EtOH. All the initiator/non-initiator thiol mixtures were prepared from 10^{-2} M solutions in EtOH of each single component. Finally, the quartz sensor was rinsed with EtOH and water, and immediately taken to the next step. Both the thiol assembly and the washing with EtOH and MilliQ water were done in the flow cell, pumping the solvents with a peristaltic pump (ISM935C, Ismatec, Zürich, Switzerland).

2.4. Synthesis of Polymer Brushes

For the brush polymerization, the sample was incubated for 5 h in a DMF–water (3:2) solution of METAC monomer–2,2-bipyridine–CuCl (molar ratio 10:2:1).

Then, the gold surfaces were consecutively rinsed in DMF–water (3:2) and water.

2.5. Salt Treatment and Counterion Exchange

Exposure of PMETAC brushes upon increasing ionic strength was performed by alternately passing through the flow cell NaCl solutions, by means of a peristaltic pump, until a plateau in the QCM-D signal was observed, and then Milli-Q water to make the brush swell back for a total recovery of the initial state.

2.6. Quantitative Evaluation of QCM-D Data

The Sauerbrey equation^[23] links frequency shifts and adsorbed masses per unit area in a very simple way:

$$m_{\text{QCM}} = -C \frac{\Delta f_i}{i} \quad (1)$$

with the mass sensitivity constant $C = 18.06 \pm 0.15 \text{ ng cm}^{-2} \text{ Hz}^{-1}$ for sensors, with a resonance frequency of $4.95 \pm 0.02 \text{ MHz}$, and the overtone number i . The normalized frequency shifts, $\Delta f = \Delta f_i/i$, for the third overtone were employed to determine m_{QCM} . This acoustic mass (m_{acous}) comprises the mass of the adsorbed polymer and the mass of the solvent that is trapped inside or hydrodynamically coupled to the polymer film. The applicability of Equation 1 is limited to sufficiently rigid films. For soft and dissipative films, more complex models would be required that account for the viscoelastic properties of the film.^[24,25] For the PMETAC brushes investigated here, we found the ratio of dissipation and normalized frequency shifts, $\Delta D/(-\Delta f)$, to be smaller than $0.2 \times 10^{-6}/\text{Hz}$, indicating that Equation 1 is a good approximation. However, in order to make a judgment on whether this value is high or low, it should be compared with the corresponding ratio expected for a semi-infinite liquid (the Kanazawa case), which compares the half-band-half width to the frequency shift.^[26] For a semi-infinite liquid, $\Delta\gamma/(-\Delta f)$ is one. The conversion from $\Delta D \times 10^6$ to $\Delta\gamma/n$ (n the overtone order) results in a factor 2.5, that is, $\Delta\gamma/n [\text{Hz}] = 2.5 \times (\Delta D \times 10^6)$. This conversion assumes a fundamental frequency of 5 MHz. Because frequency and dissipation values were already normalized by default for each overtone, n factor should not be employed in the equation. Therefore, the ratio $\Delta\gamma/(-\Delta f)$ yields results in the range 0.25–0.31 for all the brushes studied, typical of systems of a certain rigidity. This corroborated that the Sauerbrey equation is indeed a good approximation for our films, with an error below 5%. The experimental noise was typically below 2 ng cm^{-2} .

The brush thickness was further determined by applying Equation 2.

$$d_{\text{QCM}} = m_{\text{QCM}} / \rho_{\text{Brush}} \quad (2)$$

where $\rho_{\text{Brush}} = 1.0 \text{ g cm}^{-3}$ being the density of the solvated polymer film. In the pure form, the employed polymer exhibit densities between 1.0 and 1.1 g cm^{-3} , whereas the density of water or salt solutions is 1.0 g cm^{-3} . Equation 2 hence could overestimate the thickness by at most 10%.

2.7. Quantitative Evaluation of Ellipsometric Data

The bound polymer mass was determined by numerical fitting of the ellipsometric data to a multilayer model (see below). Data were fitted over the accessible wavelength spectrum, using the software CompleteEASE (Woollam). The model relates the measured ellipsometric responses, Δ and Ψ , as a function of λ , to the optical properties of the sensor surface, the polyelectrolyte brush, and the surrounding solution. The glass windows in the fluid cell were verified not to perturb the polarization of the probing light beam, and the optical properties of the sensor coating were calibrated prior to each measurement.

To extract the properties of the growing polymer chains from the ellipsometric response, a three-layer model was used. The layers represented the bulk solution, the polymer film, and the gold coating of the sensor that interact with the light beam.

The polyelectrolyte brush was treated as a single layer, which we assumed to be transparent and homogeneous (Cauchy medium), with a given thickness, d_{opt} , a wavelength-dependent refractive index, $n_{\text{Brush}}(\lambda) = A_{\text{Brush}} + B_{\text{Brush}}/(\lambda/\mu\text{m})^2$, and a negligible extinction coefficient ($k_{\text{Brush}} = 0$). A_{Brush} , B_{Brush} , and d_{opt} were fitted simultaneously. The semi-infinite bulk solution was also treated as a transparent Cauchy medium, with a refractive index of $n_{\text{sol}}(\lambda) = A_{\text{sol}} + B_{\text{sol}}/(\lambda/\mu\text{m})^2$. For water, $A_{\text{sol}} = 1.323$ and $B_{\text{sol}} = 0.00322$ were estimated from the literature.^[27] The optical properties of the sensor's coating, that is, gold layer were fixed to the values established during calibration.

The adsorbed mass per unit area was determined from de Fejter's equation:^[28]

$$m_{\text{opt}} = \frac{d_{\text{opt}}(n_{\text{Brush}} - n_{\text{sol}})}{dn/dc} \quad (3)$$

To calculate m_{opt} , we employed the refractive indices at $\lambda = 632.5$ nm, and used a refractive index increment of $dn/dc = 0.150 \text{ cm}^3 \text{ g}^{-1}$.^[29] We note that the errors associated with d_{opt} and $n_{\text{Brush}} - n_{\text{solvent}}$ can be rather high for films that exhibit only a few nanometers in thickness. We observed also that the absolute values for d_{opt} and $n_{\text{Brush}} - n_{\text{solvent}}$ are quite sensitive to minor variations in the optical properties of the solid support. When discussing our results in terms of thickness, we will therefore consider d_{QCM} rather than d_{opt} . The errors in d_{opt} and $n_{\text{Brush}} - n_{\text{solvent}}$ are though covariant, that is, the product $d_{\text{opt}} \times (n_{\text{Brush}} - n_{\text{solvent}})$ and m_{opt} can be determined with good accuracy.^[30] The experimental noise was typically below 1 ng cm^{-2} .

2.8. Quantification of the Aqueous Solvent Content

From the masses determined by QCM-D and ellipsometry, we calculate the solvent content of the film. We define hydration as the percentage of solvent contributing to the total film mass:

$$\text{Hydration}(\%) = \frac{m_{\text{QCM}} - m_{\text{opt}}}{m_{\text{QCM}}} \times 100 \quad (4)$$

3. Results and Discussion

Figure 1 illustrates, as typical example, the “in situ” combined QCM-D/ellipsometry monitoring in real time of the growth of a PMETAC brush from a 100% initiator thiol monolayer previously assembled to the gold-coated QCM-D sensor.

In Figure 1a, the variations of the acoustic parameters, frequency, and dissipation are shown as recorded by the QCM-D device. Although frequency follows a continuous decrease along the polymerization, being indicative of the progressive mass growth on top of the sensor, the dissipation increases to high values as the polymerization progresses, pointing out the formation of a film with a certain viscoelastic character. The observed relation between frequency and dissipation allows for the application

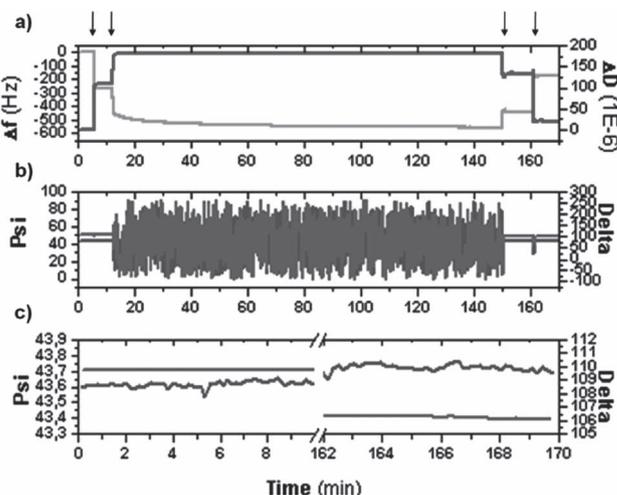


Figure 1. Synthesis of the PMETAC brush from 100% initiator-grafted gold surface followed in situ by the combined QCM-D/ellipsometry device. (a) QCM-D response, i.e., Δf and ΔD vs. time for a selected overtone ($i = 3$). (b) Ellipsometric response, i.e. Ψ and vs. Δ time for a selected wavelength ($\lambda = 632.5$ nm). (c) Magnification of the ellipsometric response at the pre- and post-polymerization states. The starting time of each solution injected is indicated by solid arrows.

of the Sauerbrey equation for the calculation of the increase in total film mass (including solvent), m_{QCM} , as the brush growth is possible.

The polymer mass, m_{opt} , was obtained from the fitting of the real-time variation of ψ and Δ measured along the PMETAC brush growth (Figure 1b). As the polymerization reaction takes place after injection of a dense color mixture of CuCl, 2,2'-bipyridyl, and METAC monomer, the light path through the chamber is blocked, which leads to a total loss of the signal reaching the detector. It can be clearly seen from Figure 1b that ψ and Δ detections turn into noise while the sample remains exposed to the solution mentioned above. After 5 h of polymerization, a consecutive rinse with DMF–water and pure water removes the monomer solution away and the optical parameters are recovered. For a better interpretation of the ellipsometric data, these were replotted in Figure 1c excluding the region where no detection is obtained. Then, the starting point and the final point of the polymerization can be easily compared to determine the total amount of polymer grown.

The calculated values at the end of the polymerization for m_{opt} and m_{QCM} and the acoustic thickness (d_{QCM}) are shown in Figure 2 as a function of the initiator density in the hybrid monolayer of thiols grafted on the surface, from 1% initiator thiol to 100%.

From Figure 2a and b, one can immediately notice the difference between the m_{acous} and optical mass (m_{opt}) and that they diverge more pronouncedly as the percentage of initiator density on the surface is increased. This is indicative

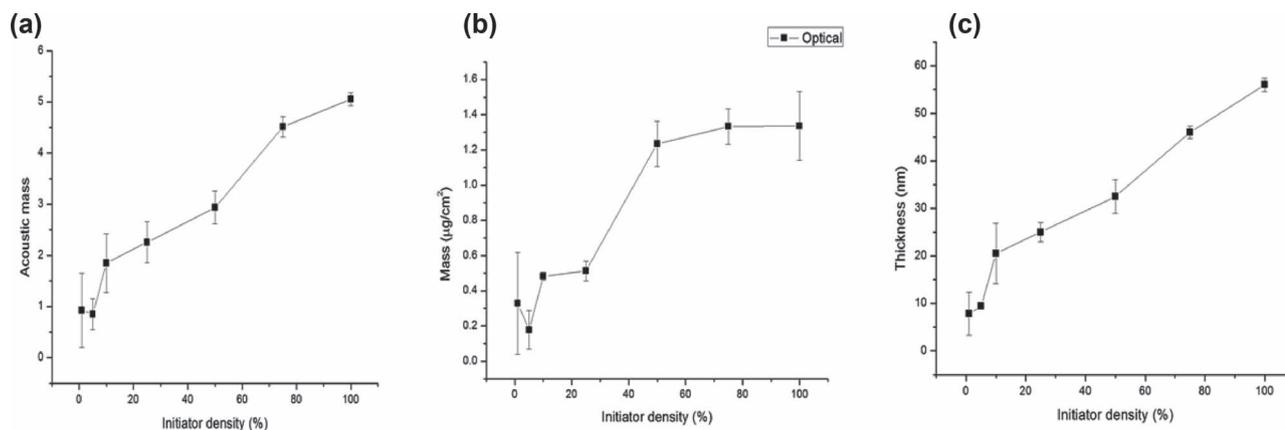


Figure 2. (a) m_{QCM} , (b) m_{opt} and (c) d_{QCM} values obtained for PMETAC brush assembled from monolayers with different initiator–blank thiol ratios.

of proportionally higher content of water in the brush as the percentage of initiator grafted is increased. Another interesting observation from this figure is that the m_{opt} of the brushes varies very slightly for initiator densities over the 50%. Indeed, when starting from 50% initiator, the final polymer mass reached is $1.32 \mu\text{g cm}^{-2}$, whereas for a brush grown from 100%, it reaches $1.47 \mu\text{g cm}^{-2}$. On the contrary, both the m_{acous} and the d_{QCM} increase, respectively, from $2.89 \mu\text{g cm}^{-2}$ and 30 nm up to $4.51 \mu\text{g cm}^{-2}$ and 50 nm. For brushes with 75% initiator density, we observe an intermediate value of thickness of 46 nm but the m_{opt} is $1.33 \mu\text{g cm}^{-2}$, which is only slightly higher than for the 50% initiator brush. This dichotomy between thickness increases over 50% and very slight changes in the polymer mass reflect a different arrangement of the polyelectrolyte chains in the brush with increasing percentage of initiator. When growing from 50% initiator, the brush has more lateral space to occupy because the number of surrounding/neighbor chains is lower. An increase in the amount of initiator in the thiol monolayer is reflected as an increase in the number of growing chains, and this will refrain the chains from occupying lateral volume. Taking into account that the masses are so similar for the three highest initiator densities, one would think that the polyelectrolyte chains are longer for the 50% initiator but at the same time they present a more coiled conformation because the thickness of the brush is smaller than for the 75% and 100% cases. However, it must also be considered that we do not know how brush density changes along the vertical direction in a brush. It is possible that at an initial state, most of the initiator molecules will lead to a growing polymer chain but after a while the accessibility of the monomers to some growing chain will be sterically limited. Hence, this will limit the growth of the brush to chains with a certain space between them that can continue growing and protrude in the solution.

Such scenario was already suggested by Cheng et al.^[31] for brushes with a high Cu(I)–Cu(II) ratio in the polymerization solution. As in our case, the synthesis takes place in the absence of Cu(II), we could consider that the growth of the brushes studied here equivalent to the conditions analyzed by Cheng et al.^[31] According to the authors, a high Cu(I)–Cu(II) ratio leads to the formation of less dense but higher molecular-weighted polymer brushes.

The difference between m_{opt} and m_{acous} corresponds to the water content of the brush, both hydration water, that is, water molecules associated with the charged monomers along the chain, and entrapped water. This water is retained in the structure in spaces between the chains and it is not associated with the monomers as hydration water. Such discrimination results very useful for a better understanding of the differences in the m_{acous} observed for the analyzed systems. For instance, when passing from a 75% to a 100% initiator-grafted brush, the m_{opt} values are so similar that we can assume that the hydration masses are pretty similar too. Therefore, the differences observed in the m_{acous} are only due to water entrapped between neighboring polymer chains.

If we consider now the brush grown from initiator densities between 10% and 50%, it can be seen how the m_{acous} shows the highest increases from around 0.5 to $1.32 \mu\text{g cm}^{-2}$, although when going from a 10% to a 25% initiator density of the PMETAC brush, almost no difference results from the optical masses. This resembles the situation observed between the 50% and 100% initiator. Decreasing the number of initiators from 25% to 10% yields a similar polymer mass, indicating the chains grow more coiled and occupy more lateral volume but at the same time they retain less water entrapped. Below the 10% initiator, and down to a 5% of initiator, both m_{acous} and m_{opt} drop significantly from 1.8 and $0.5 \mu\text{g cm}^{-2}$ to 0.85 and $0.17 \mu\text{g cm}^{-2}$,

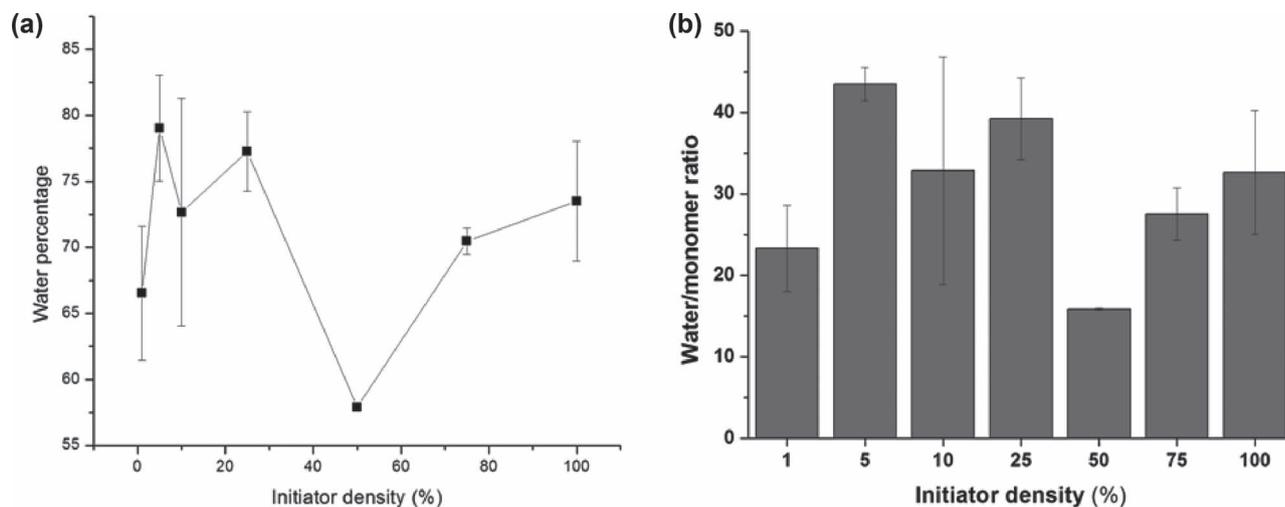


Figure 3. (a) Water content and (b) number of water molecules per METAC monomer in the brush as a function of the initiator grafting density on the surface.

respectively. For 5% and 1% initiator-grafted brushes, the m_{opt} values are also very close to each other, whereas the m_{acous} for 5% is twice the one observed for 1%.

Figure 2c shows the two linear trends followed by d_{QCM} values measured in the growth of the PMETAC brushes: a change in the initiator density from 1% to 10% makes the brush undergo a remarkable thickness increase from 4.6 to 20 nm. For brushes grown from densities over 10%, the increase in thickness follows also a linear tendency, although less steeply. d_{QCM} s of 25, 32, 46, and 50 nm are calculated for brushes grown from initiator densities of the 25%, 50%, 75%, and 100%, respectively.

Both the water content of the brush and the number of water molecules per monomer in the system have been calculated from the m_{acous} and m_{opt} values presented above, as shown in Figure 3.

Water content values in Figure 3a range between 67% and a maximum of 79% for every grafting percentage employed except for the brush grown from 50% of initiator on the surface, which yields a slightly lower hydration of around 55%. The relative limited variation in the hydration for the different percentages employed of initiator is indicating an almost constant value of hydration per monomer. If the hydration would be indeed constant it would mean that the amount of water molecules associated with each monomer is constant and independent of the density of the chains. The fact that hydration is not strictly constant is reflecting that, to a certain extent, hydration along the chain could change for the different packing in the brush monolayer. It is then worth distinguishing between water associated with the monomers forming a hydration cage and free water entrapped between the chains as mentioned above. Such differences in hydration for the different grafting densities are, from

our point of view, mostly associated with the free water entrapped. At most, the variations between samples represent around the 10% of the total hydration. This implies that most of the water in the brush is water associated with the monomers and not freely entrapped water. In this regard, we could express the total water content values in terms of water molecules per METAC monomer as shown by Figure 3b. We calculate average 23:1, 43:1, 32:1, and 39:1 ratios for 1%, 5%, 10%, and 25% of initiator-grafted brushes, respectively. Then, the value drops to 15 molecules per monomer for a brush grown from 50% of initiator and it rises back to 27:1 and 32:1 for the 75% and 100% initiator-grafted brushes. Comparable ratios of water molecules per monomer have been previously observed for highly hydrated polyelectrolyte systems.^[20]

The water content of the PMETAC brush is strongly affected by the ionic strength of the bulk washing solution in contact with the brush. Increasing the ionic strength induces a brush collapse as it is well known. During collapse, polyelectrolyte brush loose water normally.^[16] A quantitative analysis on the amount of water released upon exposure to increasing ionic strength for the PMETAC brushes studied above was done by QCM-D as plotted in Figure 4.

Figure 4a compares the frequency shifts in PMETAC brushes of variable density of initiator obtained after treatment with 0.05, 0.1, 0.5, and 1 M NaCl solutions. Exposure of the brush to salt solutions yielded positive changes in the frequency except for the PMETAC brush grown from 1% initiator, which shows a small negative shift. In all the cases, the effect in the signal caused by varying the solution density was taken into account and the frequency values stemming from it were subtracted. For brushes with initiator-grafting percentages between 5% and

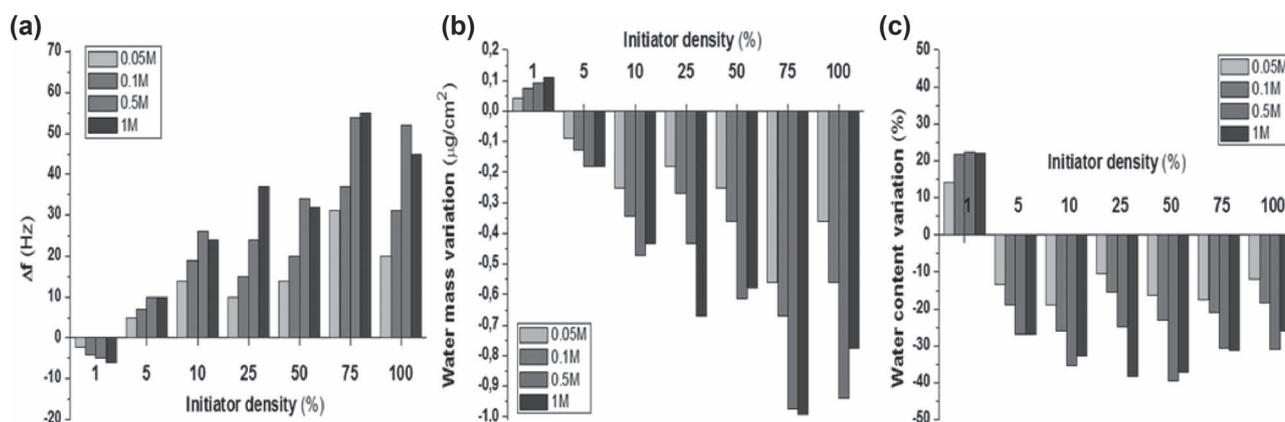


Figure 4. (a) Frequency, (b) water mass, and (c) water content percentage variations derived from treatment of the PMETAC brushes with 0.05 M, 0.1 M, 0.5 M, and 1 M NaCl solutions.

100%, the changes in absolute frequency are bigger as the amount of initiator on the surface is increased. Also frequency changes are, as expected, smaller after exposure to solutions of lower ionic strength. Frequency increases indicate water mass loss upon exposure to different ionic strengths, whereas a frequency decrease, as in the case of the 1%, would hint a mass uptake. For a better quantification of the process, the variations of mass are calculated from changes in frequency applying the Sauerbrey equation and are displayed in Figure 4b. For brushes grown from 100% and 75% initiator densities exposure to 0.05 and 0.1 M NaCl concentrations would drive to a loss of around 0.4–0.5 $\mu\text{g cm}^{-2}$ but at higher ionic strengths such as 0.5 and 1 M the brushes loose almost 1 $\mu\text{g cm}^{-2}$, which represents a 30% of the initial water content, as can be observed in Figure 4c. The percentage of water lost reaches a maximum of the 40% for the brushes grown from 50% and 25% initiator when treated with the NaCl solutions and remains constant in values around the 30% for the rest of the samples under study. The behavior shown by the PMETAC brush with 1% initiator grafted can be probably due to water molecules carried by ions diffusing through the polymer chains. The fact that the maximal loss of water for all the studied brushes corresponds to a 40% of the total hydration of the brush means that the brush does not fully dehydrate exposing up to 1 M NaCl.

Figure 5 shows how such variations in water content can be expressed in terms of water molecules per METAC monomer.

The treatment of 100% initiator-grafted brush with 1 M NaCl, for instance, reflects in a decrease of this ratio from 32:1 to 18:1, whereas the opposite situation would take place for brushes grown from 1% initiator, where the number of water molecules changes from 23:1 to up to 56:1 upon exposure to the highest ionic strength. Only at 1% initiator, the brush loses its response of losing

water when increasing the ionic strength. This change in behavior is indicative of the polyelectrolyte chains not having or having very little water entrapped that can be lost. Probably at this density of initiators, the chains are extended, coating the surface and not forming a brush as this is understood.

One could assume, because polymer chains rearrange and become closer together, that the water being primarily lost during the brush collapse corresponds to entrapped water, especially for ionic strengths below 0.1 M, but at higher ionic strengths, dehydration of the monomers should take place as well.

4. Conclusion

We have followed the growth of PMETAC brushes grown from monolayers of ω -mercaptoundecyl bromo isobutyrate thiol initiators with different densities grafted on gold

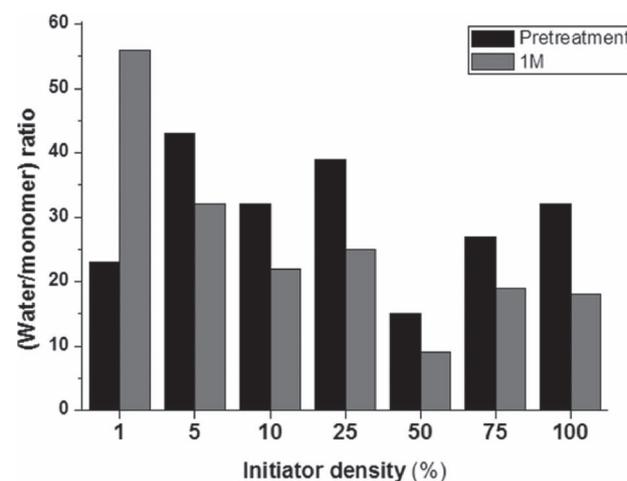


Figure 5. Water molecules per monomer of METAC at the initial/non-treated state and after exposure upon 1 M NaCl.

surfaces by spectroscopic ellipsometry and QCM-D in a single combined device. Combination of ellipsometry and QCM-D allows us to simultaneously measure dry and wet masses of the brush and, therefore, to determine the yield of polymerization and the water content of the brush. The water content of the brush was then studied as a function of the initiator density and the ionic strength of the bulk solution. Remarkably, brushes grown from a wide range of initiator percentages show an almost constant content of water. This observation implies that the water associated with the monomers represents most of the water in the brush independently of the packing of the brush chains in the brush. The small differences in water content between the different brushes must be thus due to entrapped water in the brush.

Exposure of the PMETAC brushes to increasing ionic strengths of NaCl permits calculating the amount of water released at the osmotically originated collapse. From this treatment, a removal of around 30–40% of the water in the brush is observed for 0.5 and 1 M NaCl solutions, whereas only a 10% is eliminated at ionic strengths below 0.1 M NaCl. The amount of water released would mostly come from entrapped water but changes in the hydration of the monomers can take place as well in response to high ionic strengths. However, the total dehydration of the brush cannot be reached in any case.

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- [1] M. Ballauff, O. Borisov, *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 316.
- [2] S. G. Boyes, A. M. Granville, M. Baum, B. Akgun, B. K. Mirous, W. J. Brittain, *Surf. Sci.* **2004**, *570*, 1.
- [3] Y. Tran, P. Auroy, L.-T. Lee, *Macromolecules* **1999**, *32*, 8952.
- [4] S. Edmondson, V. L. Osborne, W. T. S. Huck, *Chem. Soc. Rev.* **2004**, *33*, 14.
- [5] R. C. Advincula, W. J. Brittain, K. C. Caster, J. Rühle, *Polymer Brushes: Synthesis, Characterization, Applications*, Wiley-VCH, Weinheim (Germany) **2004**.
- [6] T. Jiang, J. J. Wu, *J. Phys. Chem. B* **2008**, *112*, 7713.
- [7] Y. Tran, P. Auroy, L.-T. Lee, *Macromolecules* **1999**, *32*, 8952.
- [8] W. T. S. Huck, *Mater. Today* **2008**, *11*, 24.
- [9] J. Bünsow, T. S. Kelby, W. T. S. Huck, *Acc. Chem. Res.* **2010**, *43*, 466.
- [10] Z. Liu, J. Liu, H. Hu, B. Yu, M. Chen, F. Zhou, *Phys. Chem. Chem. Phys.* **2008**, *10*, 7180.
- [11] S. E. Moya, O. Azzaroni, T. Kelby, E. Donath, W. T. S. Huck, *J. Phys. Chem. B* **2007**, *111*, 7034.
- [12] F. Höök, C. Larsson, C. Fant, *Encyclopedia Surf. Colloid Sci.* Dekker, New York **2002**, 774.
- [13] K. A. Marx, *Biomacromolecules* **2003**, *4*, 1099.
- [14] M. Schonhoff, V. Ball, A. R. Bausch, C. Dejugnat, N. Delorme, K. Glinel, R. von Klitzing, R. Steitz, *Colloids Surf., A* **2007**, *303*, 14.
- [15] J. B. Schlenoff, A. H. Rmaile, C. B. Bucur, *J. Am. Chem. Soc.* **2008**, *130*, 13589.
- [16] S. E. Moya, O. Azzaroni, T. Farhan, V. L. Osborne, W. T. S. Huck, *Angew. Chem. Int. Ed.* **2005**, *44*, 4578.
- [17] F. L. McCrackin, E. Passaglia, R. R. Stromberg, H. L. Steinberg, *J. Res. Natl. Bur. Stand. A.* **1963**, *67A*, 363.
- [18] P. A. Cuyppers, J. W. Corsel, M. P. Janssen, J. M. M. Kop, W. T. Hermens, H. C. Hemker, *J. Biol. Chem.* **1983**, *258*, 2426.
- [19] J. J. Iturri Ramos, S. Stahl, R. P. Richter, S. E. Moya, *Macromolecules* **2010**, *43*, 9063.
- [20] J. J. Iturri Ramos, S. E. Moya, *Macromol. Rapid Commun.* **2011**.
- [21] D. M. Jones, A. A. Brown, W. T. S. Huck, *Langmuir* **2002**, *18*, 1265.
- [22] R. R. Shah, D. Merreces, M. Husemann, I. Rees, N. L. Abbott, C. J. Hawker, J. L. Hedrick, *Macromolecules* **2000**, *33*, 597.
- [23] G. Sauerbrey, *Z. Phys.* **1959**, *155*, 206.
- [24] A. Domack, O. Prucker, J. Rühle, D. Johannsmann, *Phys. Rev.* **1997**, *56*, 680.
- [25] M. V. Voinova, M. Rodahl, M. Jonson, B. Kasemo, *Phys. Scr.* **1999**, *59*, 391.
- [26] D. Johannsmann, *Phys. Chem. Chem. Phys.* **2008**, *10*, 4516.
- [27] M. Daimon, A. Masumura, *Appl. Opt.* **2007**, *46*, 3811.
- [28] J. A. De Feijter, J. Benjamins, F. A. Veer, *Biopolymers* **1978**, *17*, 1759.
- [29] T. J. Halthur, U. M. Elofsson, *Langmuir* **2004**, *20*, 1739.
- [30] F. Caruso, K. Niikura, D. N. Furlong, Y. Okahata, *Langmuir* **1997**, *13*, 3422.
- [31] N. Cheng, O. Azzaroni, S. Moya, W. T. S. Huck, *Macromol. Rapid Commun.* **2006**, *27*, 1632.