

Explanation for the Apparent Absence of Collapse of Polyelectrolyte Brushes in the Presence of Bulky Ions

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The conformational behavior of poly[2-(methacryloyloxy)ethyltrimethylammonium chloride] (PMETAC) brushes with different chain density in the presence of large benzyltributylammonium chloride (BTBAC) ions has been studied by a Quartz Crystal Microbalance with Dissipation (QCM-D) and Scanning Force Microscopy. Dense brushes do not collapse in the presence of BTBAC solutions of increasing ionic strength, contrary to what is observed in the presence of NaCl. Brush collapse can be observed for low-ionic-strength solutions of BTBAC when the brush density has been reduced. These phenomena can be explained by considering the Hofmeister series as well as ion size and free space in the brush.

1. Introduction

Polyelectrolyte brushes consist of polymers that are attached on one end to a surface, while the other end is free, and whose monomers contain charged groups.^{1–3} The polyelectrolyte chains are in an extended or collapsed state, depending on the ionic strength of the environment.^{4–6} The extended state (the so-called osmotic brush)⁵ is characterized by stretched polymer chains, where the high counterion concentration inside the layer compared to the bulk (as a result of screening the polyelectrolytes) causes a higher osmotic pressure in the brush than in the adjacent solution. This osmotic pressure difference explains brush swelling. An increase in ionic strength leads to the reduction of the electrostatic repulsion, the so-called salted regime.^{6–9} In this regime, the difference in osmotic pressures becomes smaller and the brushes may undergo a transition toward a more coiled state. Consequently, the volume and the thickness of the brush are reduced. In addition to collapse transitions induced by the screening of electrostatic repulsions, brushes can also collapse into a precipitated state, when the counterions are replaced by ions with high affinity to the charges on the brushes, leading to overall neutral brushes.^{10,11} In both scenarios, the collapsed brushes retain a certain fraction of water, which strongly influences the mechanical properties of the collapsed films. The capability of the brushes to respond to both ionic strength and to the specific nature of the electrolytes in solution can be used for controlling the height of brushes and foresees their application as nanoactuators or controllable barriers in microfluidic devices.

In a previous paper, we observed that in the presence of benzyltributylammonium chloride (BTBAC) solutions, PMETAC brushes did not respond to the ionic strength as expected from

experiments with NaCl solutions of similar concentrations.¹² To understand the nature of this apparent insensitivity to the increase in ionic strength of the bulk solution, which is most likely related to the size and the structure of the cation, the interaction of PMETAC brushes with BTBAC and NaCl has been studied here in more detail. The brushes used in this study were grown using surface-initiated polymerization from initiator-modified (patterned) gold substrates. We studied the influence of the benzyltributylammonium cation on the brush height and hydration of stretched and collapsed brushes by comparing data obtained from Quartz Crystal Microbalance with Dissipation (QCM-D) measurements with Atomic Force Microscopy (AFM) images.

2. Experimental Details

Chemicals. Mercaptoundecane thiol, CuCl, CuCl₂, 2,2'-dipyridyl, and 2-(methacryloyloxy)ethyltrimethylammonium chloride (METAC) were purchased from Aldrich. The monomer was used as received. BTBAC was purchased from Sigma-Aldrich.

Polyelectrolyte brushes were grown from ω -mercaptoundecyl bromoisobutyrate (thiol initiator) monolayers on gold (Figure 1) using aqueous atom transfer radical polymerization (ATRP)^{13,14} as reported previously.^{15–17} The polymerization solution was prepared as follows: METAC [10 mL (75 wt % solution in water), 40 mmol] was dissolved in water (2 cm³) and MeOH (8 cm³) at 20 °C and degassed by passing a continuous stream of dry N₂ through the solution while being stirred (15 min). To this solution was added 2,2'-dipyridyl (416 mg, 2.7 mmol), Cu^I-Cl (105 mg, 1.1 mmol), and Cu^{II}Cl₂ (14 mg, 0.11 mmol). The mixture was then further stirred and degassed with a stream of dry N₂ (15 min). Initiator-coated wafer samples (~1 cm² each) were sealed in Schlenk tubes, degassed (4 × high-vacuum pump/N₂ refill cycles) and left at 20 °C under N₂. The polymerization solution was then syringed into each Schlenk tube, adding enough solution to submerge each sample completely. After various polymerization times the samples were removed, washed

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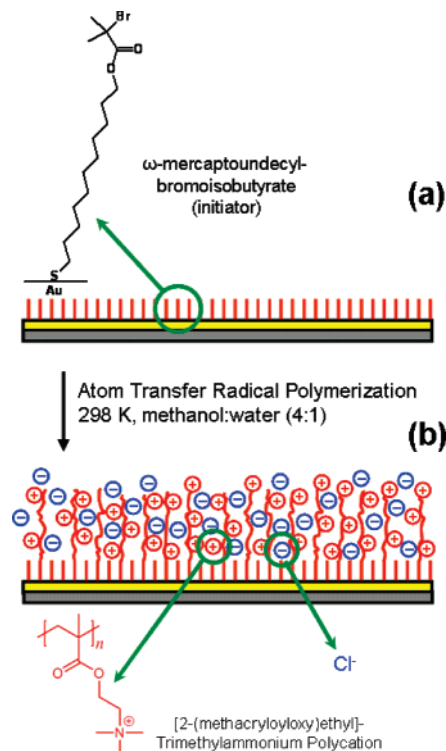


Figure 1. Schematic procedure for surface-initiated ATRP of PMETAC brushes on Au surfaces. (a) First, the initiator-terminated, self-assembled monolayers are chemisorbed on the Au surface. (b) Then, the substrates are immersed in ATRP solution containing the monomer and catalyst.

with water, then methanol, and dried under a stream of N_2 . Brush thickness was measured using a DRE ELX-02C ellipsometer with a 632.8 nm laser at a 70° angle of incidence. Patterned polymer brushes used for AFM imaging were grown from microcontact printed initiator thiols and back-filling the initiator-free areas with mercaptoundecane thiol.¹⁵ AFM experiments were carried out in a liquid cell using a MacMode PicoSPM magnetically driven dynamic force microscope (Molecular Imaging). Images were taken using commercially available type II MACLevers with a nominal force constant of 2.8 N m^{-1} at a driving frequency of 19 Hz in the liquid environment.

To prepare the initiator-coated quartz substrates, a quartz slide was washed with Milli-Q water, dried in a N_2 stream and plasma treated for 10 min. It was then immersed overnight in a solution of 50 μL of triethylamine in 30 cm^3 of dry toluene, to which was added two drops of the initiator (ω -trichlorosilylhexadecyl bromoisobutyrate). The initiator-coated substrate was then washed with toluene, then with water, then with ethanol. ATR-FTIR spectra were acquired using a Perkin-Elmer Spectrum 100 FTIR spectrometer.

Quartz Crystal Microbalance with Dissipation. Measurements were performed with a Quartz Microbalance from Q-Sense, Gothenburg, Sweden. The equipment has a chamber with 80 μL volume, which is confined on one side by the quartz crystal. The cell can be filled and the fluid exchanged using the standard Q-Sense flow system. The quartz crystals, purchased from Q-Sense, had a main resonance frequency of 5 MHz. The quartz crystal microbalance with dissipation monitoring (QCM-D) allows following changes both in frequency and dissipation in an excited quartz crystal as a function of time.^{18,19} A QCM crystal consists of a thin layer of quartz between two electrodes, through which the crystal is excited by applying an RF voltage in the region of its resonance. The eigenfrequency

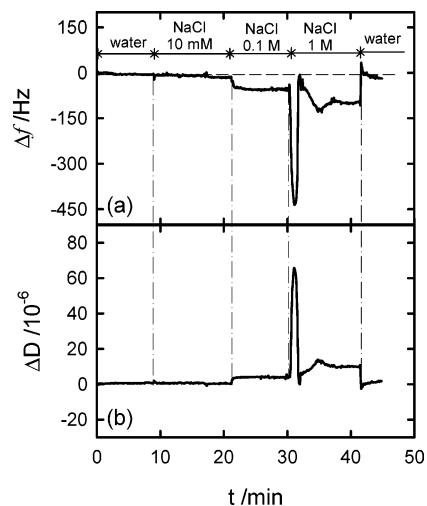


Figure 2. Changes in (a) frequency and (b) dissipation of a bare Au-coated quartz crystal after placing in contact with NaCl solutions of increasing ionic strength. (The large “spike” in both frequency and dissipation when changing to a 1 M NaCl solution is due to a temporary instability in the QCM system).

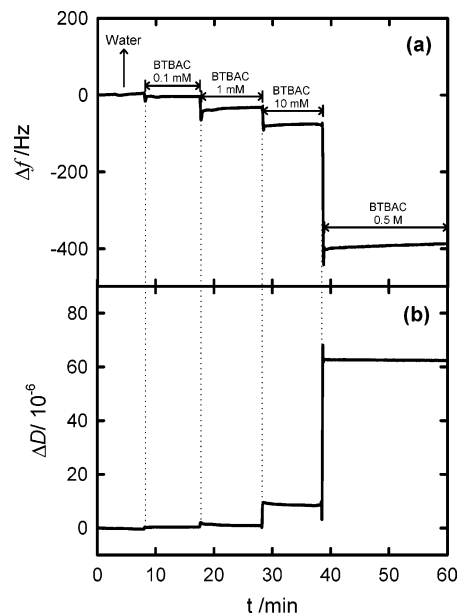


Figure 3. Changes in (a) frequency and (b) dissipation corresponding to a PMETAC-modified Au-coated quartz crystal upon exchanging the electrolytic environment from pure water to 0.1 mM, 1 mM, 10 mM, 0.5 M BTBAC, and finally pure water.

is related to the mass of the crystal. Increasing the mass adsorbed or attached to the surface of the crystal will decrease the resonance frequency. The dissipation of the crystal is measured by recording the response of the freely oscillating crystal that has been vibrated at its resonance frequency. Dissipation is defined as $\Delta D = E_{\text{dissipated}}/2E_{\text{stored}}$. The values of the dissipation are related to the viscoelasticity of the film.

Kanazawa and Gordon²⁰ proposed the following relation to quantify the frequency dependence on ionic strength:

$$\Delta f = -n^{0.5} f_0^{1.5} \left[\frac{\eta \rho}{\pi \mu_q \rho_q} \right]^{0.5} \quad (1)$$

where f_0 is the fundamental frequency, n is the harmonic number, ρ_q and μ_q are the density and shear modulus of quartz, and ρ and η are the density and viscosity of the liquid medium,

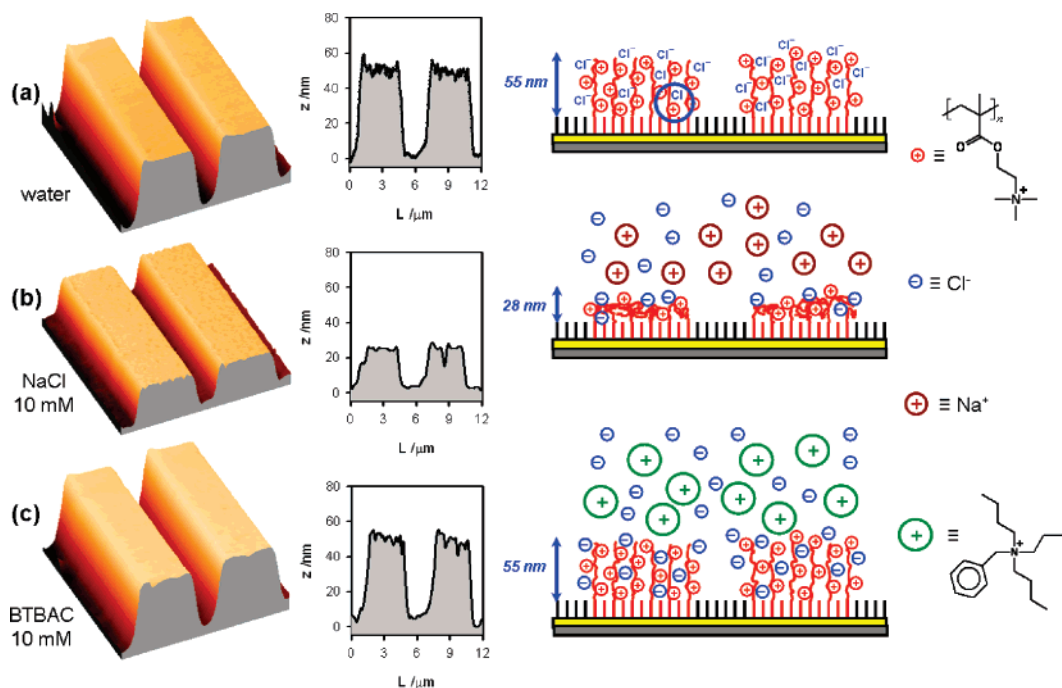


Figure 4. Three-dimensional AFM images including their cross-sectional analysis and descriptive cartoons corresponding to patterned PMETAC brushes in (a) pure water, (b) 10 mM NaCl, and (c) 10 mM BTBAC.

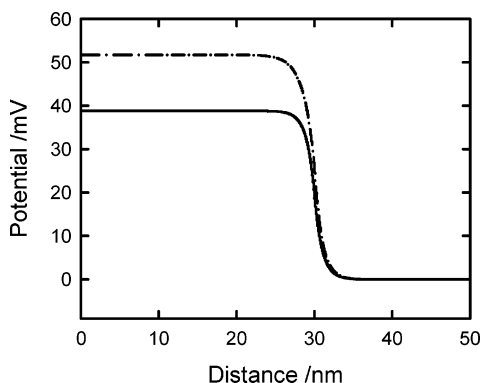


Figure 5. Illustration of the electric potential profile extending from the brush to the bulk solution. Curve 1 (continuous line): brush charged group density 300 mM/L, ionic strength 100 mM/L. Curve 2 (dashed line): same conditions as for curve 1, but co-ions are excluded from the brush interior.

respectively. The dissipation is given by

$$\Delta D = 2 \left[\frac{f_o}{n} \right]^{0.5} \left[\frac{\eta \rho}{\pi \mu_q \rho_q} \right]^{0.5} \quad (2)$$

Increasing the viscosity and density of the solution results in negative frequency shifts and an increase of dissipation. An increase in the ionic strength is equivalent to simultaneously increasing the density and the viscosity of the media, thereby complicating the interpretation of QCM-D data on collapsed polyelectrolyte brushes in high-ionic-strength environments.

3. Results and Discussion

Up to 60 nm thick PMETAC brushes (as determined by ellipsometry on “dry” films) were grown following previously reported procedures.^{9–11} Brushes were grown directly on QCM quartz crystals,^{21,22} on gold-coated silicon wafers (for ellipsometry measurements),²³ and on patterned gold-coated silicon wafers (for AFM measurements).¹⁰

Figure 2 shows the typical changes in frequency and dissipation for a gold-coated quartz crystal in the presence of a solution of increasing ionic strength and accordingly shows a *decrease* of frequency together with an *increase* of dissipation as predicted from the equations of Kanazawa. These changes are related to an increase of density and viscosity of the solution with ionic strength.

The changes caused by the expected response of the brush toward ionic strength are naturally superimposed by the effects of the density and viscosity of the solution themselves, which influence frequency and dissipation just into the opposite direction compared with the effect of the brush collapse. As previously reported, PMETAC brush-modified QCM crystals exhibited much larger and opposite shifts in both frequency (+50 Hz) and dissipation (−4 units) when placed in a 0.1 M NaCl solution.¹² The expected collapse of the brush upon increasing ionic strength is equivalent to reducing its thickness accompanied by the release of water from the interior of the brush. This decrease in the mass of the system yields an *increase* of the resonance frequency. The *decrease* in dissipation, which takes place in parallel with the thickness reduction, can be understood as the result of the conformational change from an extended and flexible brush to a collapsed and rigid one.^{10,12}

Next, PMETAC brushes were exposed to BTBAC solutions. BTBAC has the anion in common with NaCl but the cation differs quite remarkably in size, being a large organic ion species. Figure 3 shows the changes in frequency and dissipation for the PMETAC brushes in the presence of 0.1 mM, 1 mM, 10 mM, and 0.5 M BTBAC. The response is quite opposite to the one observed with the brush in the presence of NaCl. The resonance frequency *decreases* despite the addition of the salt, while the dissipation *increases*. This response seems to be indicative of the absence of brush collapse in high-ionic-strength solutions, as the frequency would then be expected to increase and the dissipation to decrease. We do note that changes in bulk viscosity could completely overwhelm the response from the brush layer, but we believe that this is very unlikely, especially for the low-ionic-strength solutions, which show the same trend.

To independently confirm the brush state as a function of ionic strength, we performed AFM measurements on patterned PMETAC brushes in different salt solutions. For all experiments, we ensured that the setpoint value used for imaging (which effectively determines the force exerted by the AFM tip on the surface) was the same, thus avoiding ambiguities in determining the height of swollen brushes. The AFM cross-sectional analysis in Figure 4 shows that in the presence of 10 mM BTBAC the brush remains fully extended ($h \sim 55$ nm), whereas the same brushes collapse to $h \sim 28$ nm in 10 mM NaCl. This observation confirms our hypothesis that the brushes do not collapse in the presence of high-ionic-strength solutions of BTBAC, which is an intriguing extension to the generally accepted model of brush collapse in high-ionic-strength solutions, regardless of the nature of the salts used.

To develop an explanation for the unexpected effect that the benzyltributylammonium cations have, we need to consider the structure and electrostatics of polyelectrolyte brushes in more detail. From the QCM-D data we can deduce that the mass of the PMETAC brushes synthesized under standard conditions is in the order of 4000 ng/cm². Considering a thickness of around 55 nm, the apparent concentration of METAC monomers in the brush film is around 3 M, corresponding to an average distance between the quarternary ammonium ions of about 0.8 nm. The brush can be considered as a rather dense polyelectrolyte solution. The overwhelming majority of the polyelectrolyte fixed charges will be compensated for by counterions, since the Bjerrum length $L_b = (e_0^2)/(4\pi\epsilon\epsilon_0kT) \sim 0.7$ nm is larger than the distance between the quarternary ammonium groups along the PMETAC chain (0.3 nm) and, even more importantly, deviations from electroneutrality inside the brush can occur only at the outer edge of the brush over a depth comparable to the Debye length. Zeta-potential measurements on spherical PMETAC brushes revealed a potential of about 50 mV in 10 mM NaCl.¹² This is consistent with a brush which is neutral in its interior and only slightly charged at its interface with the aqueous phase. From the QCM-D data further follows that the brushes release only 16% of mass as water upon collapse, further supporting the hypothesis of a rather dense PMETAC brush even if being in its extended state. Taking into account that some water may remain, we assume that the local relative dielectric constant cannot be higher than 20–40. This would result in a Bjerrum length of about 1.4–2.8 nm. Furthermore, the average distance between the quarternary ammonium ions as calculated from their concentration in the brushes is about 0.8 nm. Hence, the PMETAC brushes represent a three-dimensional polymeric material with a high density of brush ions together with their counterions located in their immediate vicinity. Upon an increase of NaCl concentration, the uncompensated charges near the brush–solution interface become more and more screened and the brush will finally collapse. The noncompensated charge near the brush solution interface is responsible for stretching the brush polymers toward the solution, thus keeping the brush extended.

To explain the absence of brush collapse in the presence of BTBAC, the large size as well as the nature of the cation has to be taken into account. Considering the density of the brushes, it might be that BTBA⁺ cations will be sterically excluded from the brush interior. The effect of this hypothetical ion exclusion on the electric potential in a brush is illustrated in Figure 5, where the electric potential $\psi(x)$ is plotted as a function of the distance x from the solid surface. The electric potential was calculated from the Poisson equation according to^{24,25}

$$\frac{d^2\psi}{dx^2} = -\frac{\rho(x)}{\epsilon_0\epsilon} \quad (3)$$

where $\rho(x)$ is the space charge density, and ϵ and ϵ_0 represent relative and absolute permittivity, respectively. The space charge density outside the brush ($x \geq d$, where d is the brush thickness) is provided by the Boltzmann distribution of the mobile ions of the electrolyte according to the potential $\psi(x)$:

$$\rho(x) = e_0 \sum_i z_i c_i^0 e^{-(z_i e_0 \psi(x))/(kT)}, \quad x \geq d \quad (4)$$

where e_0 , k , and T denote elementary charge, Boltzmann's constant, and absolute temperature, respectively. z is the charge number, and c denotes the concentration. The subscript i denotes the ion species, while the superscript 0 indicates the concentration of the i th species at infinity. Inside the brush, the space charge density includes the fixed charge density of the brush polyelectrolyte, $\rho_b(x)$, and reads as

$$\rho(x) = e_0 \sum_i z_i c_i^0 \alpha_i e^{-(z_i e_0 \psi(x))/(kT)} + \rho_b(x), \quad x \leq d \quad (5)$$

where α_i is a distribution coefficient, describing, for example, ion exclusion effects caused by the large size of the ions. For co-ions it may take any value between 0 (total exclusion) and 1 (non-limited accessibility).

The calculations in Figure 5 were performed with $\rho_b(x) = \text{const.}$, which is equivalent to a homogeneous density of the brush. The dielectric constant inside the brush was assumed equal to the bulk value of 80. This particular assumption is certainly arguable, since the high polymer density in the brush should result in a decrease of the dielectric constant. On the other hand, the high density of charged groups and thus of neutralizing counterions may result in a highly polarizable medium. The selected values of effective brush fixed-charge density have to remain arbitrary, because neither the degree of counterion condensation nor details of the dielectric structure of the brush interior are known.

The semi-numerical calculations were performed in Mathcad8 and were conducted in linear approximation, which can be justified by the high ionic strength and by the approximative nature of the assumed conditions. Nevertheless, the calculated potentials at the interface show a proper order of magnitude, and hence can serve as a qualitative means to understand the brush behavior from an electrostatic point of view. It is worth mentioning that the horizontal potential course over most of the brush interior reflects electroneutrality in the brush interior. The brush can be charged only in a small zone close to the solution interface, the thickness of which is provided by the Debye screening length (~ 1 nm in 100 mM ionic strength).

Curve 2 was derived under exactly the same premises as curve 1 except that exclusion of BTBA⁺ from the brush was assumed. This led to a larger electric potential, which is essentially equivalent to an effective reduction in ionic strength by 25% compared to curve 1. In principle, this effective ionic strength decrease caused by ion exclusion would be compatible with a retardation of the brush collapse induced by increasing salt concentration. However, the magnitude of this effect is small, and, furthermore, ion exclusion would result in an extra osmotic pressure difference between the bulk and the brush interior working toward brush collapse.

Hence the assumption of ion exclusion is not consistent with the experimentally observed behavior of the PMETAC brushes, which did *not* collapse in high-ionic-strength BTBAC solutions.

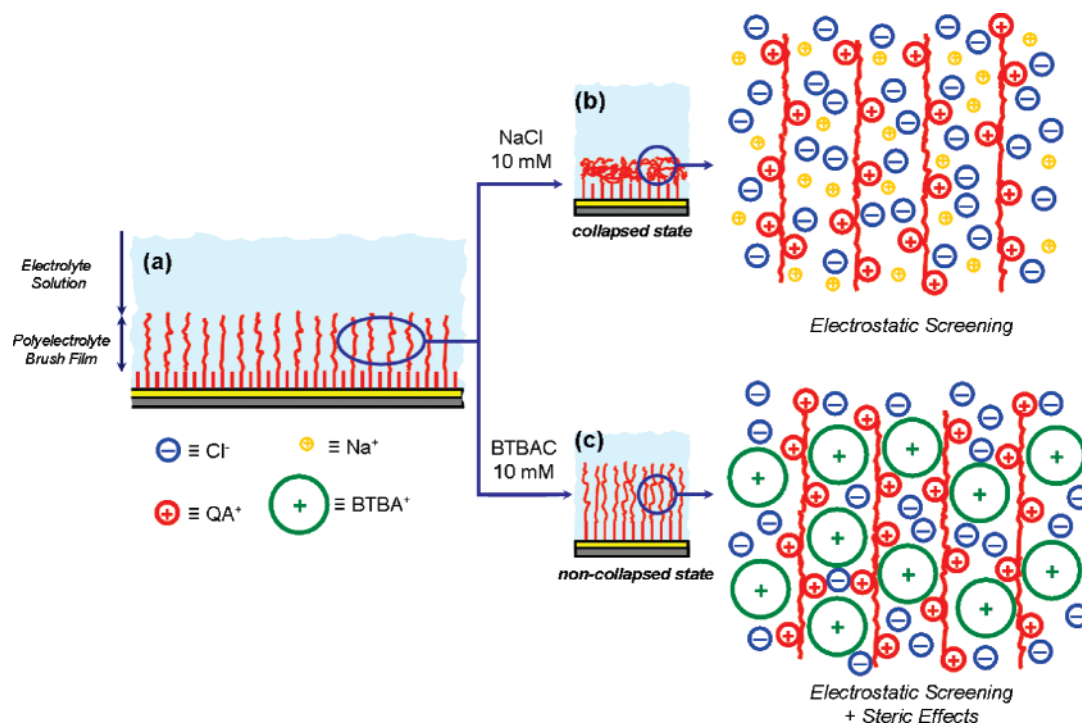


Figure 6. (a) Schematic cartoon describing the PMETAC brushes in contact with the electrolyte solution. (b) Scheme describing the inner environment of collapsed PMETAC brushes in the presence of 10 mM NaCl. (c) Scheme describing the inner environment of the non-collapsed PMETAC brushes in the presence of 10 mM BTBAC.

An alternative explanation for the experimental results would be that the large BTBA⁺ cations at least partly enter the brush interior. They may fill available space between the polyelectrolyte chains, thus preventing them from collapsing even if the ionic strength increases. As discussed above, a METAC brush polymerized from 100% initiator is already a rather dense structure. It might be possible that uptake of these bulky ions is enough to inhibit collapse by simply further reducing the free space in the brush.

Let us discuss in more detail the physical and chemical properties of the brush to consider, apart from diffusion, what other driving forces for the BTBA⁺ uptake into a region of positive electric potential may be present.

Water within the dense PMETAC brush is very likely to be different from bulk. In agreement with the Hofmeister series,²⁶ the quaternary ammonium groups along the polymer chains are only weakly hydrated. The adjacent water thus forms, compared with bulk water, an imperfect hydrogen-bonded network, similar to water near hydrophobic moieties. The chemical potential of such water should be larger than the chemical potential of bulk water as a result of missing hydrogen bonds of the former. To compensate for this chemical potential difference, the concentration and hence the density of the water near the brush polymers will be slightly decreased. In addition, the carbonyl oxygen and the ester oxygen of the side chains have each two nonbinding electron pairs very likely interacting with water molecules and thus further disturbing the water structure.

BTBA⁺ cations are also quaternary amines and, like METAC⁺, they have a structure-breaking effect on water. They are ionic chaotropes and thus partition into low-density water. From this point of view, the interior of the brush provides an entropically more favorable environment for BTBA⁺ than the bulk solution. In addition to the effect of the solvent (water) structure, van der Waals interactions between the polymer and the organic cation may also contribute to the attraction of the organic cation toward the brush constituents. The suggested hypothesis of

entropy-driven interaction of BTBA⁺ ions with the brush interior preventing collapse of the brush finds an analogy in the interaction of perchlorate ions with PMETAC brushes.¹² Perchlorate showed an enhanced affinity to the brush. In terms of the osmotic concept of the brush, perchlorate has to be considered as an ion species which due to its tendency of exclusion from water inside the brush does not fully contribute to the osmotic pressure. It will induce precipitation of the brush by increasing hydrophobic interactions and hinder the brush to re-swell by decreasing the osmotic pressure in the brush. This explains why it is difficult to wash the perchlorate away. The common feature of perchlorate and BTBA⁺ is that both ions are chaotropic, stabilizing low-density water and increasing hydrophobic interactions. In the presence of perchlorate anions, the brush collapses; in the case of BTBA⁺, the brush has lost its ability to collapse. We assume that this difference in behavior must be related to the size of the BTBA⁺ ions. The BTBA⁺ cations are bulky and probably prevent the chains from changing conformation and collapsing. Because of their size, the BTBA⁺ ions may replace the volume of the structured water present along the polymer chains. The cartoon in Figure 6 sketches the behavior of a PMETAC brush in NaCl and BTBAC, both 10 mM.

In the figure are also indicated the ionic species with different colors: blue, chloride anions; yellow, sodium cations; green, benzyltributylammonium (BTBA⁺); and red, the quaternary ammonium (QA⁺)-bearing groups of the PMETAC brushes. The sizes of the different species are scaled assuming that the edge length of the BTBA⁺ tetrahedron (1 nm) is three times the diameter of the chlorine ion and five times the sodium ion and that the edge of the BTBA⁺ is slightly larger than the distance between METAC groups in the brush (approx. 0.8 nm).

The specific BTBA⁺–brush interaction should lead to retention of the ion within the brush. To test if this indeed took place, we performed IR experiments. To test if ion retention was taking place, we performed IR experiments. IR spectra of Figure 7

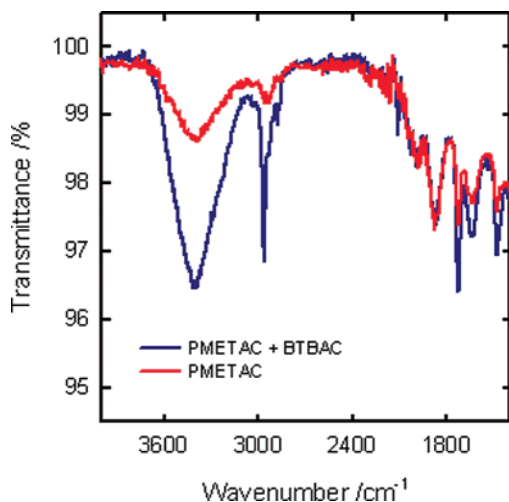


Figure 7. IR spectra of dried PMETAC brushes and PMETAC brushes treated with BTBAC for 3 h previous to the drying, both synthesized on quartz.

were both recorded in the dry state: (a) PMETAC brushes dried from a water solution, and (b) the same brushes previously immersed in 0.1 M aqueous BTBAC for 3 h, then washed with Milli-Q water to remove any surface BTBAC, and dried. The spectra differ in the much more significant intensity for (b) than (a) of the peak around 2900, characteristic of C–H stretching, and in the peak in the 3200–3500 region, which results from hydrogen-bonded water. The higher intensity of these peaks for (b) speaks of a significant concentration of the BTBA⁺ ions in relation to the monomer concentration of METAC. On the basis of separate calibration studies (not shown) for both the IR signals of the brushes and the BTBAC, we estimate a loading of 2 equiv of BTBAC per quaternary ammonium side group in the brush. The significant result of these experiments is that indeed there is ion penetration in the brush and the affinity of the BTBA⁺ for the environment triggers their retention even though the sample has been carefully washed.

To further test the suggested hypothesis, we decided to study METAC brushes with a lower grafting density. The amount of initiator was reduced to 25% in the thiol monolayer, and the other 75% was made up by blank thiols. In the synthesized brush, the individual polymer chains would have more lateral space and the content of normally structured free water is increased in relation to the case when 100% initiator was used for synthesizing the brush.

Figure 8 presents the changes in frequency and dissipation of the reduced in density PMETAC brush upon addition of BTBAC. The frequency increases and the dissipation decreases when the external solution was exchanged from water to 1 mM BTBAC. The changes became even more pronounced when the concentration of BTBAC was increased to 10 mM. The QCM-D data prove that collapse does indeed take place. The explanation is that although BTBA⁺ ions may partition into the low-density water of the brush, ionic-strength-induced collapse takes place, because there is sufficient structured water available between the more diluted polyelectrolyte chains to be released upon the interaction between the collapsing chains.

In view of the discussed Hofmeister series related effects of ions on the brush state it is worth considering that NaCl is known as a destroying agent of low-density water on the surface of proteins and polymers. It thus may destabilize the hydration layer on the polyelectrolyte surface. This may be a significant contribution to the brush collapse in addition to the osmotic/ionic strength-related change of brush state.

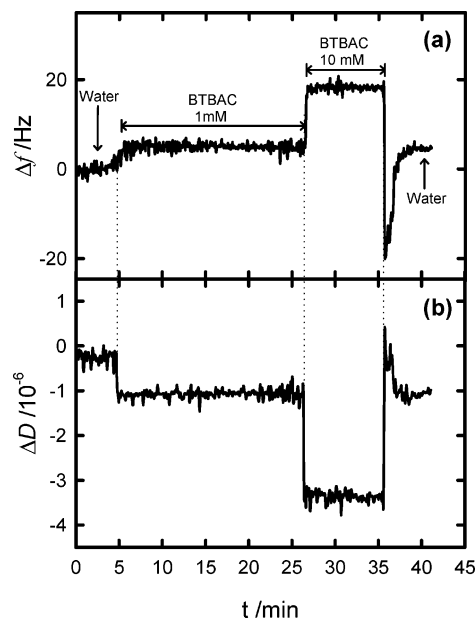


Figure 8. Changes in (a) frequency and (b) dissipation corresponding to PMETAC brushes synthesized from 25% thiol initiator in the presence of BTBAC solutions of different ionic strengths.

4. Conclusions

The quartz crystal microbalance in combination with AFM can be used to study the complex phenomena of polyelectrolyte brush collapse. It has been found that in presence of a large ion like BTBA⁺ dense polyelectrolyte brushes loose their capability to collapse in response to ionic strength. This behavior can be understood from entropic and steric considerations, taking into account the state of water in the brush and the size of the ions. This is a novel finding demonstrating further possibilities to control and fine-tune the brush state by size and type of the background electrolyte co-ion. The findings also show the complexity of a brush system where important parameters such as water content and state have hardly been studied in the context of brush structure transitions.

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