

Switching the Properties of Polyelectrolyte Brushes via “Hydrophobic Collapse”

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ABSTRACT: We have studied the changes in physical and chemical properties of cationic poly(2-(methacryloyloxy)ethyltrimethylammonium chloride) brushes after collapse driven by ion-pairing interactions in the presence of ClO₄⁻ anions. Results derived from the quartz crystal microbalance technique, atomic force microscopy, Fourier transform infrared spectroscopy, and contact angle goniometry indicate that ion-paired collapsed polyelectrolyte brushes suffer a dramatic loss of water accompanied by conformational changes leading to markedly different mechanical properties. This scenario is completely different from polyelectrolyte brushes whose collapse is simply driven by pure Coulombic screening, for example, in the presence of Cl⁻ anions. In addition, wetting measurements indicated that ion-pairing interactions can be used to switch surface characteristics from hydrophilic to hydrophobic in a reversible manner. The immediate implications of these experimental results are related to the promising use of polyelectrolyte brushes as biolubricants and the design of “smart” surfaces exhibiting ion-sensitive reversible changes in interfacial properties.

Introduction

Polyelectrolyte brushes are ideal building blocks for soft nanotechnology and the engineering of surfaces. Changes in ionic strength, pH, or solvent properties can lead to markedly different surface properties¹ (surface energy, hydration, charge distribution) due to the transitions between (fully) stretched and (nearly) collapsed states of the polymer brushes.^{2,3} As a consequence, these “soft” films have demonstrated an ever-growing relevance within diverse technological fields ranging from smart responsive surfaces to biomedical devices. This is the case for surface-grafted 2-(methacryloyloxy)ethylphosphorylcholine (MPC), a monomer which bears charged quaternary ammonium and phosphate groups that is widely used as a coating in intravascular stents or soft contact lenses.⁴

The well-known collapse of polyelectrolyte brushes in salt solutions is generally described as the result of a significant screening of the charges on the pendants groups.⁵ However, in addition to this electrostatic screening of charges, the presence of ions can result in specific interactions between the ions involved and the charged monomers of the brush, as recently reported in the literature.^{6–9} These studies have demonstrated that the ionic environment of charged polymer brushes can dramatically influence the properties of these surface-confined macromolecular systems, such as lubrication and compressibility.¹ The introduction of chemical triggers for collapse (rather than merely relying on ionic strength) will allow the development of surfaces with a responsive behavior that can be exploited in sensors as well as actuating mechanisms in fluidic devices.

In this work we have investigated the critical role of ion-pairing interactions on the collapse of strong cationic

polyelectrolyte brushes. In general, behavior of polyelectrolyte brushes has been studied with variations in pH, ionic strength, or temperature. In our case, we show and discuss the valuable role of ion-pairing interactions on tailoring the characteristics of these surface-confined systems. We observed that in the presence of specific ion-pairing interactions the nature of the electrically neutral polymer can be sharply switched from hydrophilic to hydrophobic. This change in the chemistry of the monomer units leads to a collapse driven by hydrophobic interactions with the surrounding water. As a consequence, ion-paired collapsed polyelectrolyte brushes show very compact stiff structures markedly different from similar brushes whose collapse is driven by pure Coulombic screening. In particular, these findings could have remarkable implications on the promising use of polymer brushes as biolubricants on artificial joints¹⁰ where the polymer hydrophilicity plays a determinant role in the reduction of wear.

Experimental Section

Patterned Samples Preparation. Microcontact printing (μ CP) of a thiol initiator onto clean gold substrates, following a procedure used within our group,^{11,12} produced patterned gold surfaces ready for polymerization. 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^ICl (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 with water and then methanol, and dried under a stream of N₂.

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Spherical Brushes Preparation. Cab-o-sil M-5 grade, untreated fumed silica was obtained from Cabot Corp. with an average particle (aggregate) length of 0.2–0.3 μm . The synthesis of the trichlorosilane ATRP initiator, 2-bromo-2-methylpropionic acid 3-trichlorosilylpropyl ester, was adapted from published procedures¹³ utilizing allyl alcohol. Cab-o-sil M5 (1 g), trichlorosilane initiator (75 μL), dry triethylamine (Et_3N) (500 μL), and dry toluene (40 cm^3) were stirred under N_2 for 19 h at room temperature. The particles were then filtered and washed with toluene and acetone and dried under high vacuum. To grow PMETAC from these particles, a PMETAC polymerization solution was prepared (as described above) and injected over initiator-coated particles (0.1 g) under N_2 . Polymerization was left to proceed for 23 h. After polymerization the solution was centrifuged to concentrate the particles. The supernatant was removed and replaced with clean MeOH to wash the particles. Mixing and centrifugation with MeOH was repeated three times to wash the particles. After the final supernatant removal the PMETAC-coated particles were dried under high vacuum and stored under N_2 until needed. PMETAC brushes grown on SiO_2 were 25 nm thick, and the diameter of the PMETAC-modified particles was 192 ± 15 nm, as determined by dynamic light scattering.

Contact Angle Measurements. Contact angle goniometry was performed using a homemade stage with a computer-controlled microsyringe and digital camera. Infusion and withdrawal rates of 4 $\mu\text{L min}^{-1}$ were used. Advancing water contact angles (θ_{AW}) were recorded.

Fourier Transform Infrared Spectroscopy. FTIR spectra were recorded with a BioRad spectrometer using PMETAC brushes grown on silicon wafers. Spectra were taken with a resolution of 4 cm^{-1} by accumulating 128 scans on each run. The sample compartment was carefully purged with nitrogen to reduce the interference of water and carbon dioxide absorption from the gas phase.

ζ -Potential Measurements. The ζ -potential of the spherical PMETAC brushes was measured using a ZetaSizer NanoSeries (Malvern, UK). Each value was obtained by taking the average of at least four measurements. The ζ -potential was estimated from the electrophoretic mobility, u , using the Helmholtz–Smoluchowski equation:

$$u = \epsilon\zeta/\eta \quad (1)$$

where η and ϵ are the viscosity and the dielectric constant of the medium, respectively.

Atomic Force Microscopy. 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. For probing the mechanical properties we have studied the influence of the applied force on the topographic characteristics¹⁴ of the patterned brushes as obtained from the AFM images. We measured the change on the tip penetration with the applied force, i.e., the cantilever oscillation amplitude, A . First, we imaged a $10 \times 10 \mu\text{m}^2$ area of the patterned sample at low load, i.e., at A_0 . Then, we continuously increased the applied load by decreasing the A/A_0 ratio; that is, the cantilever oscillation amplitude normalized to the initial value (low load). Finally, we widened the scanned area up to $20 \times 20 \mu\text{m}^2$ at A_0 in order to check that no permanent damage was induced on the scanned area by the AFM imaging at high loads.

Quartz Crystal Microbalance with Dissipation. QCM-D measurements were performed using a Q-Sense microbalance (Sweden) at 21 $^\circ\text{C}$. Commercially available (Q-SX-301, Q-Sense) gold-coated quartz crystals were used.

Results and Discussion

Scanning force microscopy has been extensively used for studying surface/mechanical properties of thin polymer films like hydrogels, fiber-reinforced composites, or biological materials¹⁵ and for studying the switching of

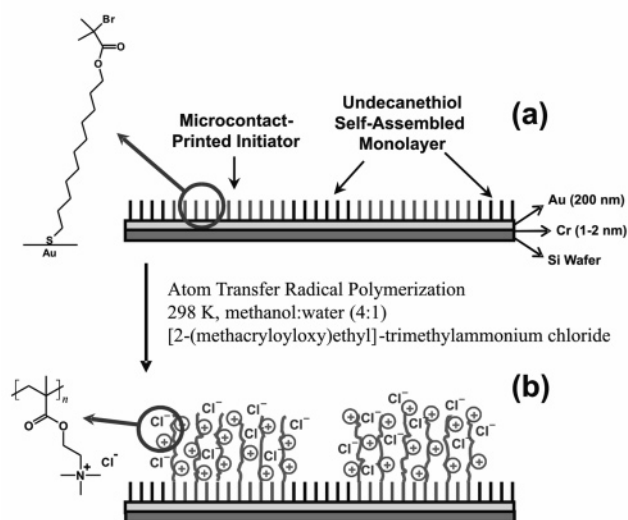


Figure 1. Scheme showing the patterned growth of PMETAC brushes. (a) Microcontact printing of the initiator thiol molecules and backfilling with undecanethiol. (b) Growth of PMETAC brushes in the patterned regions by atom transfer radical polymerization.

properties in binary polymer brushes.¹⁶ The mechanical behavior of collapsed polyelectrolytes, such as their elasticity or response to a deforming stress, can give valuable information about the actual polyelectrolyte environment in the collapsed state. In this work, we have studied the mechanical properties of collapsed PMETAC brushes using a patterned configuration on gold substrates (Figure 1). The reason for choosing this configuration is the common observation of “substrate effects” during indentation experiments, in particular when dealing with sub-100 nm thick films.¹⁷ Using a patterned configuration, it is much easier to estimate the “real” magnitude of the indentation on the polymer brush since a single scan depicts the hard substrate (reference level) and the indented/penetrated polymer brush under the same imaging conditions. The patterned polymer brushes were prepared by microcontact printing as described in the Experimental Section, following a method reported previously.^{18,19}

Patterned PMETAC brushes were first imaged by TM-AFM under low-load conditions. A “dry” thickness (L) of 23 ± 3 nm was measured (it should be noted that these brushes are hygroscopic and without special precautions; they will contain some water); when measurements were repeated under water, an extended conformation ($L = 55 \pm 4$ nm) was observed in accordance to what is expected for a surface-tethered polyelectrolyte in the presence of a “good solvent”.⁵ When varying AFM imaging conditions from low load to high load, drastic changes in the phase image (Figure 2a) and the “measured” brush height (topographic image) (Figure 2b) were seen. This was thought to be a consequence of the considerable indentation and/or penetration of the AFM tip into the polyelectrolyte brush. For this case the “measured” brush height (h) was 7 nm and can be interpreted as a penetration depth (d) of 48 nm. This result is reasonable if we consider the soft character of the extended PMETAC brush, which corresponds to the extensively reported indentation/penetration effects of AFM probes on soft surfaces (Figure 3) that have been in the literature for many years.²⁰ However, it must be noted that in the case of polymer brushes AFM measures penetrability rather

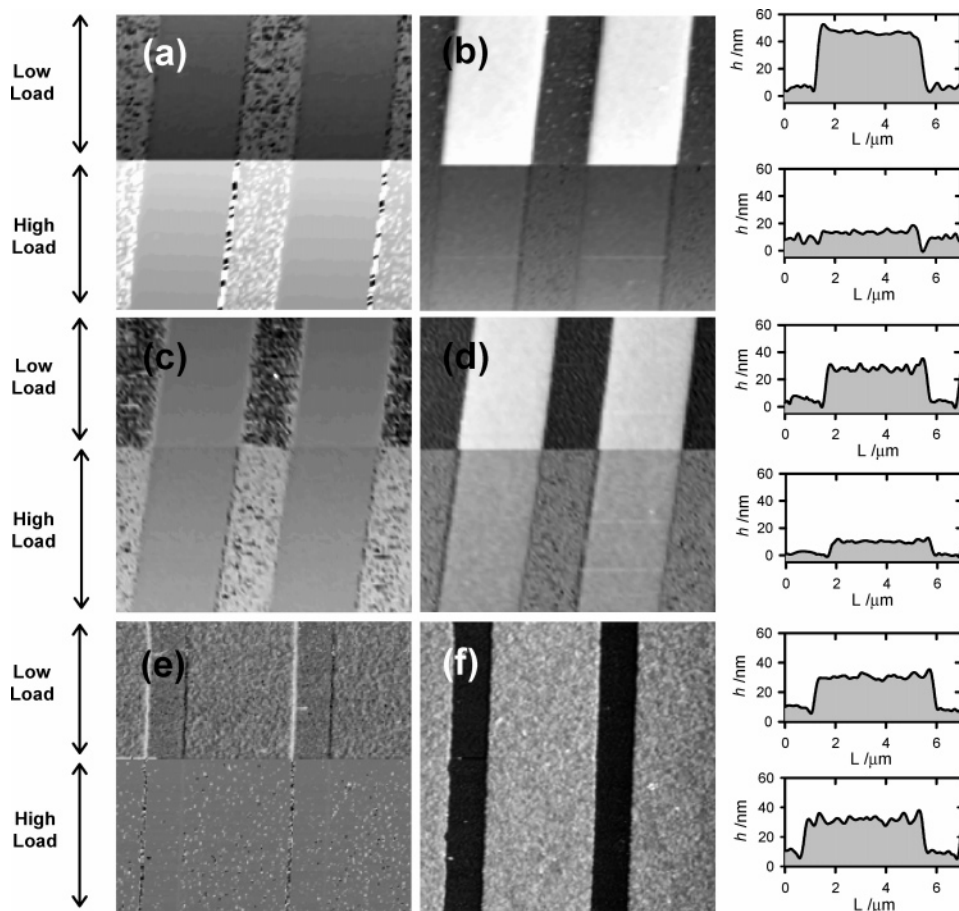


Figure 2. TM-AFM imaging under liquids of patterned PMETAC brushes with their respective topographic cross-sectional analysis: (a) phase and (b) topographic image when scanned under H_2O at low and high loads, (c) phase and (d) topographic image when scanned under 1 M NaCl at low and high loads, (e) phase and (f) topographic image when scanned under 1 M LiClO_4 at low and high loads. Low and high loads correspond to $A/A_0 \rightarrow 1$ and $A/A_0 \sim 0.3$, respectively.

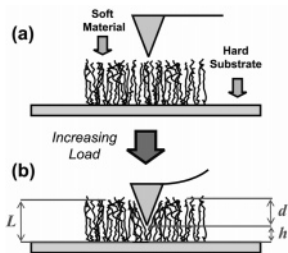


Figure 3. Simplified scheme depicting (a) scarce brush penetration when scanning at low loads and (b) significant brush penetration when scanning at high loads.

than stiffness as demonstrated in detail by Frisbie and co-workers.²¹

Similar behavior (penetration effect) was observed when the same TM-AFM experiments were performed on PMETAC brushes in an aqueous 1 M NaCl solution (Figure 2c,d). In the presence of 1 M NaCl the PMETAC brush is collapsed, $L = 29 \pm 3$ nm (measured under low-load conditions), as a consequence of the significant screening of the pendant charges in the polyelectrolyte brush by the electrolyte solution. AFM imaging of the PMETAC brush under high-load conditions in the same electrolytic environment clearly shows evidence of tip penetration, since the measured h was 11 nm, which means that the AFM tip penetrated into the collapsed brush a distance corresponding to ~ 18 nm (d).

A remarkable difference was observed when similar AFM experiments under liquids were carried out in the

presence of an aqueous 1 M LiClO_4 solution (Figure 2e,f). PMETAC brushes imaged under low-load conditions in the presence of 1 M LiClO_4 solution showed a collapsed conformation but with a brush thickness slightly lower, $L = 22 \pm 3$ nm, than that observed in 1 M NaCl. This slight change in L when cationic brushes are collapsed under the same ionic strength conditions but in the presence of different anions has been recently observed.²² Substantially increasing the load during imaging resulted in a clear change in the phase image, but surprisingly no topographic changes were detected ($h = 22 \pm 3$ nm). This invariant behavior on brush thickness after a considerable increase in load implies that the AFM tip did not penetrate the PMETAC brush. This fact clearly shows that a drastic change upon brush stiffness occurs in the presence of ClO_4^- but not in the presence of Cl^- counterions. Figure 4 presents the AFM-measured penetration depth (d) as a function of the load (represented by A/A_0) for NaCl and LiClO_4 solutions. This plot shows in more detail the significant change in stiffness of the PMETAC brush in the presence of different electrolytes. Under 1 M NaCl (brush in collapsed conformation) changes in tip load (A/A_0) from 1 to 0.6 are associated with d values of up to ~ 20 nm. Conversely, similar increasing loads promote no significant change in d on the ClO_4^- -coordinated PMETAC brush, even in the A/A_0 range from 0.5 to 0.3. For similar applied loads brushes coordinated with ClO_4^- showed a nearly constant penetration depth, even at low A/A_0 . TM-AFM experiments under 10^{-3} M LiClO_4 and 10^{-3}

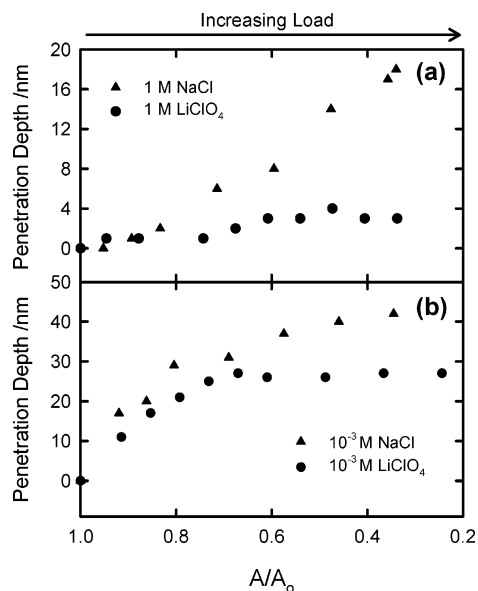


Figure 4. Representation of the penetration depth as a function of the applied load (A/A_0) for PMETAC brushes in (a) 1 M NaCl (\blacktriangle) and 1 M LiClO₄ (\bullet); (b) 10⁻³ M NaCl (\blacktriangle) and 10⁻³ M LiClO₄ (\bullet).

M NaCl showed similar trends in stiffness to those obtained at higher concentrations (Figure 4b).

This experimental evidence certainly indicates that the change in the stiffness is closely related to changes in the ionic environment within the PMETAC brush. In other words, under comparable ionic strengths using monovalent electrolytes, the PMETAC is not penetrated or easily indented when coordinated with ClO₄⁻; this is in clear contrast to PMETAC coordinated by Cl⁻ anions, where the AFM tip penetrates the brush in a manner similar to that in pure water. Amazingly, this sensitive effect of the counterion is still observed at relatively low ionic strengths (10⁻³ M).

In accordance with this observation, it has been recently reported that the mechanical properties of polyelectrolyte multilayers are quite sensitive to the nature of the counterion.^{23,24} These authors found that the stiffness of polyelectrolyte multilayers could be varied according to the counterion chosen, with a trend following the Hofmeister series.²⁵ Thus, the interaction of quaternary ammonium ions, which constitute the pendant groups in a PMETAC brush, with the surrounding counterions (anions) plays a major role in determining the characteristics of the polyelectrolyte brush. In contrast to hydrated Cl⁻ anions, ClO₄⁻ anions are scarcely hydrated, large, and highly polarizable species; consequently, they can interact very strongly with the quaternary ammonium pendant groups through ion-pairing interactions,²⁶ promoting differences in the physicochemical properties of the polyelectrolyte brush. As observed in solvent extraction, large anions with low hydration energies preferentially coordinate large, hydrophobic cations over smaller anions with higher hydration energies.²⁷ We have performed ζ -potential measurements on silica nanoparticles modified with PMETAC brushes (also known as "spherical brushes", see Experimental Section). The ζ -potential for spherical PMETAC brushes in 0.1 M NaCl was +26.7 mV in contrast to the +7.9 mV measured on similar brushes in 0.1 M LiClO₄. When working at ionic strengths as low as 10⁻⁴ M, the ζ -potential changes from +44 to +22 mV when changing from NaCl to LiClO₄. The ζ -potential

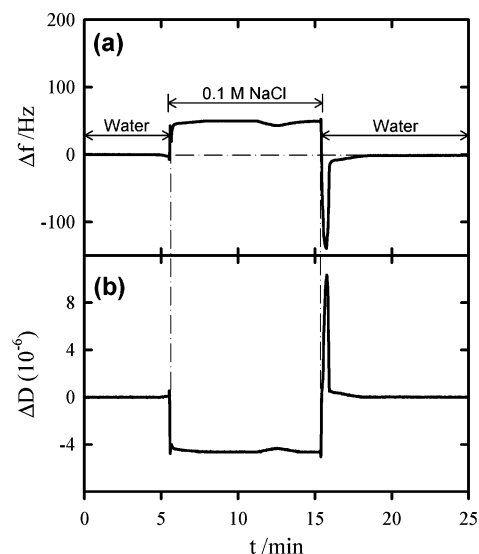


Figure 5. Quartz crystal microbalance response on (a) frequency and (b) dissipation when METAC brushes are placed in 0.1 M NaCl and then washed with pure water.

depends on the space distribution of counterions, which is responsible for the appearance of a net charge on the particles (though electroneutrality holds). A decrease in ζ -potential changing from NaCl to LiClO₄ for equal surface density of charged quaternary ammonium groups means that ClO₄⁻ anions are more tightly bound to the brush surface than Cl⁻ species. Light scattering experiments indicated that the presence of ClO₄⁻ anions in solution triggered aggregation or agglomeration of the spherical brushes, while in the presence of Cl⁻ anions they remained dispersed. This experimental observation is in agreement with a lower ζ -potential and a reduced stability of the colloidal dispersion. Similar observations have been recently reported by Mie and Ballauff for spherical brushes in different ionic environments.⁷

The differences in the electrostatic environment and the brush collapse introduced by ion-pairing effects were also monitored by changes in frequency and dissipation measurements on a quartz crystal coated with a PMETAC brush using a quartz crystal microbalance with dissipation (QCM-D).²⁸ Dissipation (defined as $\Delta D = E_{\text{dissipated}}/2E_{\text{stored}}$) is a measure of the capacity of the system to release the mechanical energy and provides information on the rigidity of the film. Let us first consider the case of changing water for a NaCl solution. Figure 5 shows an increase in frequency and a decrease in dissipation when the electrolytic environment of Cl⁻-coordinated PMETAC brushes (as synthesized) is changed from pure water to 0.1 M NaCl. We interpreted the increase in frequency as a loss of water molecules from the polyelectrolyte brush during the collapse process.

The decrease in dissipation can be understood as a change from a rather soft polymer film to a more rigid collapsed structure, in addition to the change in the viscoelastic coupling of the polymer to the solution. However, we must note that these changes cannot be entirely attributed to the change in the brush conformation, since there is a concomitant change in solution viscosity upon solvent exchange (water to 0.1 M NaCl) that is also sensed by QCM. When the PMETAC brushes are next placed into pure water, the frequency and dissipation values return to the original ones. This observation indicates that the original environment of

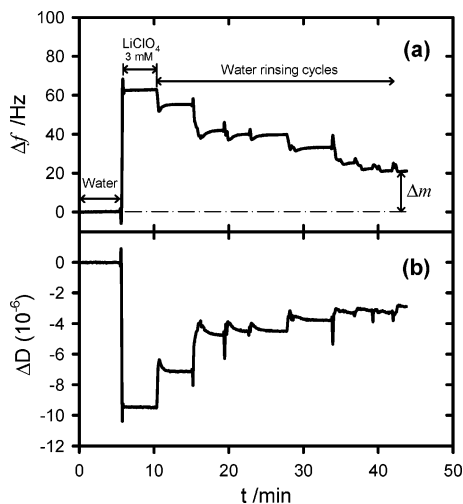


Figure 6. Quartz crystal microbalance response on (a) frequency and (b) dissipation of METAC brushes in 3 mM LiClO_4 followed by repeated rinsing cycles with pure water.

the Cl^- -coordinated PMETAC brushes in water, in their extended conformation, can be easily restored by simply flushing water over the polyelectrolyte brush removing the 0.1 M NaCl solution. The excess of NaCl is easily removed from the inner environment of the PMETAC brushes, leaving only Cl^- counterions responsible for fulfilling the electroneutrality condition. A completely different scenario was observed on QCM-D experiments with dilute LiClO_4 solutions. Changing from water to 3 mM LiClO_4 an increase in frequency and a decrease in dissipation can be observed for the same PMETAC brushes. Like in the case of NaCl solutions, these changes can be associated with a loss of water during collapse and conversion to a more rigid brush state, respectively.

Replacing the dilute LiClO_4 solution by water inside the QCM chamber is followed by only a slight decrease in frequency and an increase in dissipation. Even though frequency and dissipation reach a plateau after nine cycles (Figure 6), their original values are not restored, thus implying a significant change in the brush characteristics when coordinated by ClO_4^- species. The staircase-like signals for frequency and dissipation indicate that removal of electrolyte in excess, of that required for electroneutrality, is much more difficult than in the case of NaCl, showing that the affinity of ClO_4^- anions to the brush chemical/ionic environment is remarkably different. After the frequency reaches a plateau, the fact that Δm does not reach zero indicates a loss in mass when comparing the brush to the starting conditions under water. If we consider that ClO_4^- anions (FW: 99.5) are heavier than Cl^- species (FW: 35.5), this mass variation indicates a significant loss of water molecules from inside the polyelectrolyte brush, which can be associated with a rather hydrophobic environment. This fact could also explain the slow release of "hydrophobic" ClO_4^- anions,²⁹ as depicted in Figure 6. This interesting phenomenon of preferential retention of scarcely hydrated ions on a nonpolar matrix has been previously described by Rydall and MacDonald on the basis of NMR studies of anion binding to neutral lipid membranes.³⁰ This significant change in the water content of the polymer brush is also reflected in the wetting characteristics of the PMETAC-modified surface. Water contact goniometry shows a θ_{AW} of 37° for the Cl^- -coordinated brush (Figure 7a) and a θ_{AW} of 79°

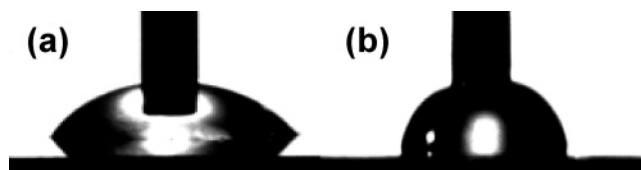


Figure 7. Change in wettability for a Au surface modified with PMETAC brushes when their corresponding counterions are (a) Cl^- and (b) ClO_4^- .

for the ClO_4^- -coordinated brush (Figure 7b). Thus, PMETAC-modified substrates change from moderately hydrophilic to moderately hydrophobic when the counterion is changed from Cl^- to ClO_4^- .

Referring back to the QCM-D trace, after several washing cycles when the dissipation reaches a plateau, the relative diminution on dissipation from the initial state before ion treatment describes a more rigid state of the polyelectrolyte brush *in pure water* when coordinated with ClO_4^- counterions. This observation corroborates AFM experiments on comparable surfaces, indicating that ClO_4^- -coordinated PMETAC brushes retain their collapsed conformation and their stiff characteristics when probed under water. Thus, ion-pairing interactions are strong enough to be used to change the properties of polyelectrolyte brushes in such a manner that they cannot be reverted even when the inner ionic environment of the brush is diluted. Clearly, QCM-D and contact angle measurements indicate that the hydration of polyelectrolyte brushes is sharply changed upon coordination of ClO_4^- , giving the monomer units hydrophobic characteristics. This can be easily understood if we consider the fact that ClO_4^- salts of quaternary amines are water-insoluble compounds but highly soluble in chloroform or xylene.^{26,27} Within the traditional picture of polyelectrolyte brushes, the collapse is seen as a result of electrostatic screening of pendant charges by means of highly mobile counterions.^{31–34} However, in the case of the ion-paired ClO_4^- species the brush experiences not only an electrostatic change but also a drastic chemical change (hydrophilic–hydrophobic). As a consequence of this change, the brush suffers what we call "hydrophobic collapse" instead of the traditional "electrostatic-driven collapse". We use the term "hydrophobic collapse" due to the close resemblance to the protein folding mechanism driven by hydrophobic interactions.³⁵ Brushes ion-paired with ClO_4^- anions behave like neutral brushes in a poor solvent, where the monomers try to exclude the solvent and effectively attract one another. As a consequence, the flexible chains form a compact globule^{36,37} that minimizes the interaction between the ion-paired monomers and the solvent. As suggested by recent theoretical results reported by Winkler et al., ion-pairing effects in polyelectrolytes should be associated with the appearance of dipole moments (monomer–counterion).³⁸ These attractive dipole–dipole interactions are responsible for the collapse of the whole chain into very compact structures. Earlier theoretical work by Khokhlov and co-workers indicated that condensation of counterions and the formation of ion pairs could significantly influence the conformation of the polyelectrolyte chain.^{39,40}

Recently reported electron paramagnetic resonance spectroscopy experiments⁴¹ showed that tightly bound or site-bound species (like ion-paired ClO_4^- anions) can promote large changes in the collective motion of polyelectrolyte chains when compared to mobile or territorially bound species (like Cl^- anions). In the case of our

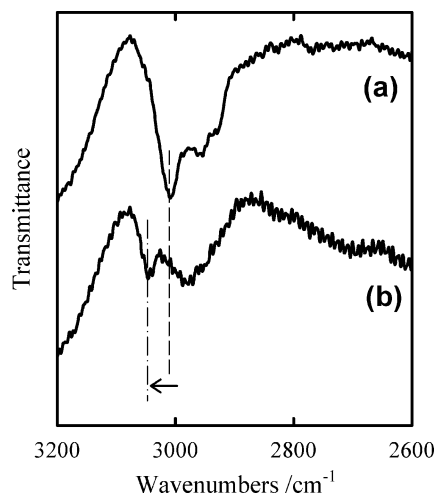


Figure 8. FT-IR spectra in the 3200–2600 cm^{-1} region corresponding to PMETAC brushes coordinated by (a) Cl^- and (b) ClO_4^- anions. The frequency shift marked with an arrow between the dotted lines corresponds to $\sim 35 \text{ cm}^{-1}$.

PMETAC brushes we observed a marked blue shift ($\sim 40 \text{ cm}^{-1}$) in the IR signals encountered in the region 3100–2900 cm^{-1} when the counterion was changed from Cl^- to ClO_4^- (Figure 8). In the Cl^- -coordinated brushes these signals correspond to the asymmetric (3017 cm^{-1}) and symmetric (2944 cm^{-1}) methyl stretching modes of the quaternary ammonium headgroups, $\text{CH}_3-(\text{N}^+)$, the asymmetric stretching band (2959 cm^{-1}) of the terminal methyl group, and the antisymmetric CH_2 stretching mode (2918 cm^{-1}).^{42–44}

These blue shifts clearly reflect the strong interaction between ClO_4^- anions and the quaternary ammonium groups. In addition, considering that the CH_2 stretching modes are very sensitive to conformational order of hydrocarbon chain⁴⁵ (showing a shift to higher frequencies when conformational disorder is increased), we can assume that ion-pairing of ClO_4^- anions introduces conformational changes to the polyelectrolyte chains of the brush. This observation is closely related to recently reported studies demonstrating that scarcely hydrated anions can introduce significant disorder to LB monolayers of octylamine spread over the electrolyte solutions.⁴⁶

In the case of PMETAC brushes these changes can be described as a more disordered state, probably due to a large number of entangled and interpenetrated “neutral” chains in a necklace-like or globular conformation. This picture describing the new conformational state of stiff ClO_4^- -coordinated brushes is in close agreement with recent theoretical models describing the behavior and flexibility of polyelectrolytes in poor solvents^{47,48} and with recently reported AFM studies performed by Minko et al. on poly(2-vinylpyridine) single molecules.⁴⁹

Another key point when dealing with the chemical/ionic environment inside polyelectrolyte brushes concerns the reversibility of the changes introduced inside the brush. As previously discussed, strongly bound ClO_4^- species are not easily displaced from the polyelectrolyte brush. In our case, to reverse the ion-paired configuration, we washed with a concentrated NaCl solution to obtain the original environment (Cl^- -coordinated PMETAC). The excess of Cl^- should displace the equilibrium ClO_4^- /quaternary ammonium in the brush, restoring the original chemical/ionic environ-

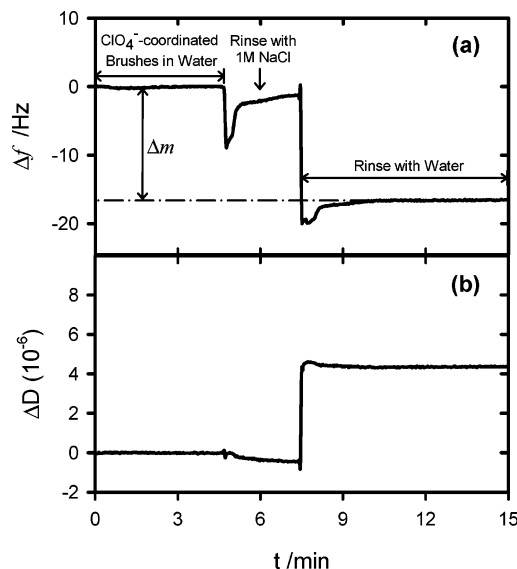


Figure 9. Quartz crystal microbalance response on (a) frequency and (b) dissipation of ClO_4^- -coordinated PMETAC brushes when rinsed with 1 M NaCl and then with pure water. The horizontal dotted line indicates the original frequency of the as-synthesized (Cl^- -coordinated) PMETAC brushes before introducing any change on their ionic environment.

ment. We followed this process with QCM-D (Figure 9). First, a ClO_4^- -coordinated brush was washed thoroughly with pure water until the QCM trace reached a plateau. After a few minutes a 1 M NaCl solution and then water were flushed into the QCM chamber.

The QCM-D trace revealed that the frequency and dissipation values changed back to the original ones upon completion of washing (horizontal dotted lines in Figure 9), indicating that the strongly bound ClO_4^- counterions were displaced by Cl^- anions and the original brush chemical composition was restored. These changes inside the brush were also monitored by FTIR (Figure 10) with the aim of obtaining information about the anionic species involved in the different states of the polyelectrolyte brush. The IR spectrum (between 2000 and 1000 cm^{-1}) of an as-synthesized Cl^- -coordinated PMETAC brush shows typical distinctive IR signals corresponding to C=O stretching (1709 cm^{-1}), C–H bending (1487 cm^{-1}), and C– N^+ stretching (1260 cm^{-1}) characteristic of quaternary ammonium groups and the Si–O asymmetric stretching mode corresponding due to the silicon wafer (1118 cm^{-1}).^{42–44} Placing the PMETAC brush in 0.1 M LiClO_4 solution for 15 min followed by careful rinsing with pure water and drying shows the appearance of a new signal at 1104 cm^{-1} in the IR spectrum, corresponding to Cl–O stretching⁵⁰ of the ClO_4^- anions inside the brush. Subsequent submersion of the substrate in pure water for 40 min shows a decrease in ClO_4^- content. In fact, the $I^{(\text{C}=\text{O})}/I^{(\text{Cl}-\text{O})}$ signal ratio changes from 3.2 to 2.4, indicating that ClO_4^- in excess is retained in the brush even when carefully rinsed and removed after further washing.

FTIR measurements indicate that the excess ClO_4^- , beyond that needed for electroneutrality, can be removed with prolonged washing cycles as previously deduced from QCM experiments. Submersion of the ClO_4^- -coordinated PMETAC brushes for 20 min in 1 M NaCl shows complete disappearance of the IR signal corresponding to Cl–O stretching, implying that all the tightly bound ClO_4^- anions were effectively displaced by Cl^- in the brush. This again agrees with the data

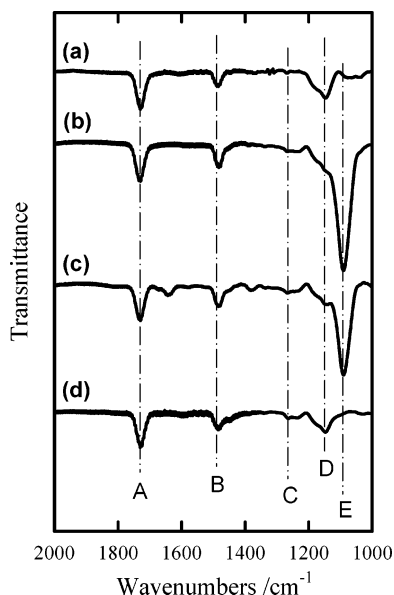


Figure 10. Fourier transform infrared spectra in the 2000–1000 cm^{-1} region corresponding to (a) as-synthesized Cl^- -coordinated PMETAC brushes, (b) PMETAC brushes immersed during 15 min in 0.1 M LiClO_4 and carefully rinsed with water, (c) PMETAC brushes immersed for 15 min in 0.1 M LiClO_4 , carefully rinsed with water, and then placed in pure water for 40 min, and (d) ClO_4^- -coordinated PMETAC brushes immersed for 20 min in 1 M NaCl . IR signals assigned from A to E are referred to in the text.

obtained by QCM which indicates a replacement of ClO_4^- ions by Cl^- .

Conclusions

Polyelectrolyte brushes bearing quaternary ammonium cationic groups undergo ion-pairing interactions in the presence of scarcely hydrated anions, in close resemblance to the well-known Hofmeister series. These polyelectrolytes show a favorable affinity to water while charged but upon ion-pairing the polyelectrolyte chains suffer a sharp hydrophilic-to-hydrophobic change that expresses itself as a collapse to a very compact state. In addition, this change is accompanied by conformational transitions of the surface-confined polyelectrolytes when switching from a well-solvated state to a poorly solvated one. The ion-paired hydrophobic collapsed state is markedly different from a brush collapsed due to screening effects under high ionic strength conditions. The surprising change in stiffness is attributed to an interplay between conformational changes in polyelectrolyte backbone and a significant decrease in water content upon ion-pairing, brought about by the hydrophobic character of the ion-paired monomer units. This fact reflects the critical role of the counterion⁵¹ on determining the degree of hydration and as a consequence the behavior and characteristics of the polyelectrolyte brush.⁵² These results could have immediate implications on biomedical applications of surface-grafted polyelectrolytes, particularly to those related to the use of polyelectrolyte films as artificial biolubricants where polymer hydration is a key factor.⁵³

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References and Notes

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