

NANOSCALE LOCKING AND UNLOCKING OF POLYELECTROLYTE BRUSHES FOR THE FABRICATION OF RESPONSIVE SURFACES

Moya S.

1 Centro de Investigación en Química Aplica (CIQA), Blv Enrique Reyna 140, 25100 Saltillo, Coahuila.
smoya@ciqa.mx

2 Nanoscience Centre, University of Cambridge, J.J Thompson Ave, West Cambridge, Cambridge, UK.

Abstract- 2-(Methacryloyloxy)ethyl-trimethylammonium chloride brushes P(METAC) were synthesised in situ in a Quartz Crystal Microbalance with Dissipation (QCM-D) chamber. The whole synthesis could be followed from the adsorption of the thiol initiator to the washings with different solvents after the polymerization. The fabricated brushes were then studied in different ionic conditions to explore their capability of response in the nanoscale combining QCM-D and Scanning Force Microscopy (SFM). It was observed that it was possible to obtain irreversible collapse if the brushes were treated with ions capable of establishing specific interactions such as MgSO_4 or LiClO_4 . The first seems to induce the formation of a network in the polymer film by acting as a crosslinker and a collapsed state in water after the treatment, associated with a high wetting performance. The ClO_4^- ions show higher affinity than the Cl for the pendant quaternary ammonium groups resulting in the replacement of the latter, with a subsequent loss in water content and increase film rigidity.

Introduction

Atom transfer radical polymerization (ATRP) is a simple and effective method of polymer synthesis which provides a narrow molecular weight distribution under easily controllable reaction conditions and has been extensively used for the fabrication of brushes. Although polymer brushes grown by ATRP have been well characterized post-synthesis, there is a lack of knowledge about the initiator adsorption on the surface and the kinetics of the polymerization process. One common way of measuring the kinetics of growth for brushes is to polymerize several samples simultaneously and stop them at different times to measure the thickness by either ellipsometry or AFM, relying on the assumption that the polymerization conditions and the amount of initiator are equal for all the samples. These measurements cannot be performed in real time on a single sample.

An interesting case among polymer brushes are those, whose polymer chains have repeatedly charged units, the so called polyelectrolyte brushes. The chains are, depending on the solvent, in an extended or collapsed state. In water, contrary to the situation in an electrolyte solution at sufficiently high ionic strengths, the intra and intermolecular electrical repulsion will result in an extended conformation, with fully hydrated charged monomers. Increasing ionic strength leads to the reduction of the electrostatic repulsion and can thus induce the collapse of the brush, which will lose water and reduce its thickness. Besides the collapse with ionic strength, the charged monomers in the brush can interact specifically with certain ions, this interaction is restricted to the particular chemistry of the monomers and ions. Combining the effects of changing ionic strength with specific interactions wide spectra of phenomena can be expected from the brush.

The capability to respond to ionic strength and to collapse by specific interactions can be used for controlling the height of brushes in devices and foresees their application as nanoactuator or controllable barriers.

The kinetic of growth of polyelectrolyte brushes and their possibilities as nanoactuators in relation with the counter ion environment and the ionic strength are the subject of this paper. To address these problems it has been made use of the Quartz Crystal Microbalance with Dissipation (QCM-D), as main research tool.

Experimental Part

Chemicals and Brush Synthesis

Mercaptoundecane (blank thiol), $\text{Cu}^{\text{I}}\text{Cl}$, $\text{Cu}^{\text{II}}\text{Cl}_2$, 2, 2'-dipyridyl (bipy) and [2-(methacryloyloxy)ethyl] trimethylammonium chloride (METAC) were purchased from Aldrich. The monomer was used as received. γ -mercaptoundecyl bromoisobutyrate (thiol initiator) was synthesized..

For the ARTP reaction a mixture of two parts solvent (80% methanol, 20 % water) and one part of monomer was flushed with N_2 for one hour. $\text{Cu}^{\text{I}}\text{Cl}$, $\text{Cu}^{\text{II}}\text{Cl}_2$ and bipy were then added to the solution in the following molar proportions: $[\text{METAC}]: [\text{Cu}^{\text{I}}\text{Cl}]: [\text{Bipy}]: [\text{Cu}^{\text{II}}\text{Cl}_2] = 100:2:5:0.1$. Microcontact printing (μCP) of a thiol initiator onto clean gold substrates produced patterned gold surfaces ready for polymerization.

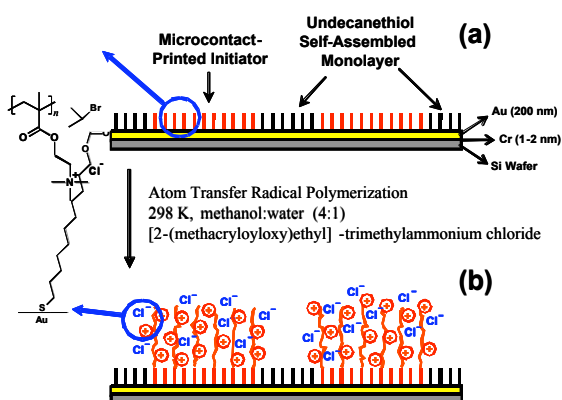


Figure 1. Scheme showing the patterned growth of PMETAC brushes. (a) Microcontact printing of the initiator thiol molecules and backfilling with undecanethiol. (b) Growth of PMETAC brushes in the patterned regions by Atom Transfer Radical Polymerization.

Quartz Crystal Microbalance with Dissipation

Quartz crystal microbalance with dissipation (QCM-D) allows to follow process which involve a change of the mass attached to the crystal by recording changes in both frequency and dissipation of an excited quartz crystal as a function of time. A QCM-D crystal consists of a thin layer of quartz between two electrodes; the crystal is excited applying an RF voltage across the electrodes near the resonance frequency. The frequency of oscillation is related to the mass of the crystal, additions of mass to the surface of the crystal will decrease the frequency. The dissipation of the crystal is measured by recording the response of the freely oscillating crystal that has been vibrated at its resonant frequency. The values of the dissipation are related to the viscoelasticity of the film. All measurements were performed on a quartz microbalance from Q-Sense, Gothenburg, Sweden. The dissipation is defined as $\Delta D = E_{\text{dissipated}}/2 E_{\text{stored}}$. The equipment has a chamber with an 80 μl volume, which is closed at 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, have a main resonance frequency of 5 MHz.

Results

Fig.2 shows the changes in frequency and dissipation on a quartz crystal during the polymerization process in the chamber. The QCM trace begins with the adsorption of

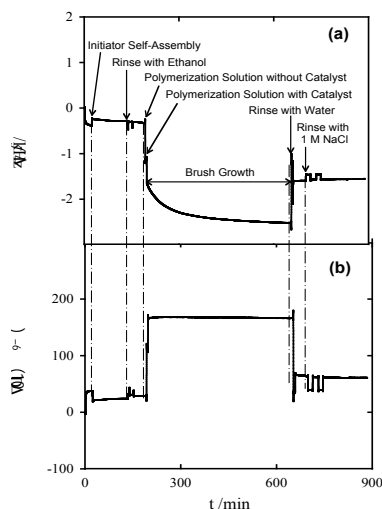


Figure 2. Changes in a) frequency and b) dissipation of a quartz crystal during assembly of a monolayer of 100 % thiol initiator and the subsequent METAC polymerization and rinsing.

the thiol initiator on the gold coated surface, through to the addition and removal of the polymerization solution and ends with the washings of the sample. The first part of the graphs corresponds to the adsorption of a γ -mercaptoundecyl bromoisobutyrate thiol from a 5 mM ethanolic solution. The process of thiol adsorption was followed for over 3 hours, and then the sample was washed with ethanol, water and 1 M NaCl (aq).

For the polymerization reaction, the chamber was filled with a mixture of 2 parts solvent (methanol: water, 80:20) and 1 part monomer solution, which had been deoxygenated by flushing with nitrogen for one hour. This stage was followed by the addition of the same deoxygenated mixture but with the catalyst ($\text{Cu}^{\text{I}}\text{Cl}$, $\text{Cu}^{\text{II}}\text{Cl}_2$) and ligand (bipy) added. The polymerization reaction was left to run till completion, which occurs when the frequency and dissipation reach a plateau. The chamber was then washed with methanol, then water and finally with 0.1 M NaCl (aq) to assure that the brush is free from ligands, catalyst and excess monomers.

The METAC polymerisation shows an initial rapid increase as can be seen by the steep changes in frequency and dissipation. This stage is followed by a slower increase in rate for the frequency and an almost immediate plateau for the dissipation. The apparent mass increase after the polymerization, calculated using the Sauerbrey equation, is of the order of 4400 ng/cm^2 . This mass is not only associated with the polymer brushes grown from the substrate, but also the mass of the water retained in the film.

The QCM-D technique can be also used to monitor the collapse of the brush with increasing ionic strength. Fig. 3a shows the changes in frequency and dissipation for the brush synthesised on the gold coated quartz crystal when the ionic strength of the solution is increased from water to 1 M NaCl. Increasing ionic strength results in an increase of the frequency values and a decrease of the dissipation, changes, which are reversible when going back to water. The increase of the frequency must be due to the loss of water during collapse and the diminish in dissipation can be interpreted as the brush changing conformations from a viscoelastic state when extended to a collapsed

state where it behaves more like a solid. In Fig.3b we observed the AFM micrographs corresponding to the brush in water, 1 M NaCl and finally in water again. The change in height during collapse is approximately 30 nm.

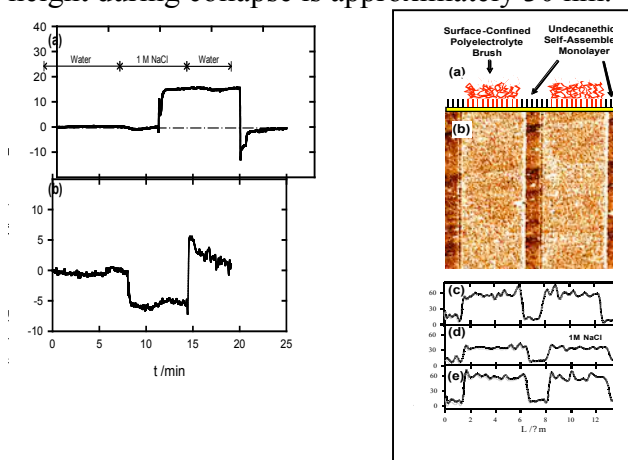


Fig.3.1 Quartz Crystal microbalance response on a) frequency (a) and dissipation (b) when METAC brushes are in presence of 1 M NaCl.

Fig. 3. 2(a) Scheme of the patterned polymer brushes chemisorbed on a gold surface. B) AFM image of patterned METAC brushes under water. C) Cross-sectional analysis derived from AFM imaging of METAC brushes under water. D) cross-sectional analysis of patterned METAC brushes imaged under 1 M NaCl. E) Cross-sectional analysis of METAC brushes under water after being placed in 1 M NaCl.

Next, the interaction of the PMETAC brushes with MgSO_4 and LiClO_4 was studied. When the brushes were studied with the QCM-D in presence of high concentrations of MgSO_4 (0.5 M) and then washed with water, the frequency and dissipation values of the system were those of a collapsed state as shown for NaCl (higher frequency and lower dissipation than the initial state), Fig.4a. To obtain again the original values of frequency and dissipation as in water the system had to be washed first with 1 M NaCl and then with water. The AFM micrographs confirm the state of collapse for the brush in water after the treatment with MgSO_4 . We assume that the SO_4^{2-} could be generating a state of crosslinking in the brush among quaternary ammonium groups and perhaps with the Mg^{+2} as well. This collapsed state has the particularity of being extremely hydrophilic, probably because the MgSO_4 are retained in the polymer layer.

The case of LiClO_4 is a different one, when the brushes become in contact with the ions ClO_4^- , which has more affinity for the quaternary ammonium groups than the Cl^- ions replace these. The ClO_4^- ions are bulkier than Cl^- and have a strong screening effect on

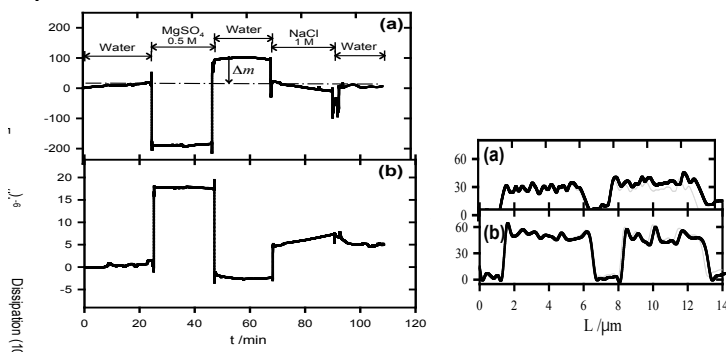


Fig. 4. 1 Quartz crystal microbalance response on (a) frequency and (b) dissipation when METAC brushes are placed in different electrolyte environments (0.5 M MgSO_4 and 1 M NaCl)

Fig. 4.2 Cross-sectional analysis, derived from AFM imaging performed *under pure water*, corresponding to: (a) patterned METAC brushes placed in 0.5 M MgSO_4 during 20 minutes, and (b) patterned METAC brushes placed in 0.5 M MgSO_4 during 20 minutes, rinsed with water and then placed during 30 minutes in 1 M NaCl.

harder than the previous one. The state of collapse with LiClO_4 induces as well retention of ions, which can be released only after several washings with water in a progressive way. Like with MgSO_4 to return to the original chemical state is necessary to apply a washing with a solution of high concentration NaCl . Water contact goniometry shows a θ_{AW} of 37° for the Cl^- coordinated brush (Fig 5a) and a θ_{AW} of 79° for the ClO_4^- coordinated brush (Fig 5b). Thus, PMETAC-modified substrates change from moderately hydrophilic to moderately hydrophobic when the counterion is changed from Cl^- to ClO_4^- .

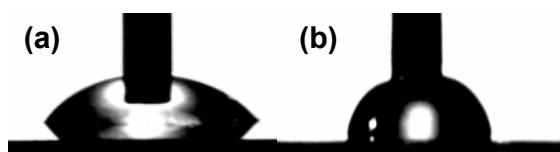


Figure 5. Change in wettability for a Au surface modified with PMETAC brushes when their corresponding counterions are: (a) Cl^- and (b) ClO_4^- .

Conclusions

It is possible to follow the growth of brushes with the QCM-D obtaining valuable information about time of reaction and amount of material synthesized.

PMETAC brush is capable to response to different salts by specific interactions and with the ionic strength, resulting in states of different thickness, wetting and mechanical properties. It is possible to make the brush hydrophilic in a permanently collapsed state under water by using MgSO_4 and to make more hydrophobic and harder with LiClO_4 . The ClO_4^- replace the Cl^- resulting a new brush structure with different water content and chain conformation while the MgSO_4 .

Bibliography

S. Moya, O.Azzaroni, T. Farhan, V. Osbourne, W.T.S.Huck *Angewandte Chemie Int. Edit* (2005) 44 (29) 4578-4582 "Locking and Unlocking of Polyelectrolyte Brushes: Towards the Fabrication of Chemically Controled Nanactuators"..

S.E. Moya, A.A.Brown, O.Azzaroni, W.T.S.Huck *Macromolecular Rapid Communications*. (2005) 26, 1117-1121 "Following Polymer Brush Growth Using Quartz Crystal Microbalance"