Electronic Supplementary Information

Surface Confined Self-Assembly of Polyampholytes Generated from Charge-Shifting Polymers

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Summary

Material and methods

Chemicals

Poly(ethyleneimine) (PEI, M = 750,000 g/mol, CAS 9002-98-6), poly(sodium 4-styrene sulfonate) (PSS, M = 70,000 g/mol, CAS 25704-18-1), poly(allylamine hydrochloride) (PAH, M = 56,000 g/mol, CAS 71550-12-4), sodium nitrate ($NaNO_3$, CAS: 7631-99-4), hydroquinone (M = 110.11 g/mol, CAS: 123-31-9) and potassium hexacyanoferrate(II) (M = 422.41 g/mol, CAS 14459-95-1) were purchased from Sigma-Aldrich. Deuterated water was purchased from Eurositop and DCl from Sigma-Aldrich. All chemicals were used as received. Polyelectrolyte solutions were prepared at 1 mg/mL by dissolution of the adequate amount in 150 mM $NaNO_3$ aqueous solution adjusted at pH 5.

Synthesis of PAHc

Citraconate-modified poly(allylamine hydrochloride) (PAHc) was prepared according to Lynn and coll. (*Soft Matter*, 2008, **4**, 1688-1695). PAHc solution was prepared in 150 mM $NaNO_3$ with 60 mM Hydroquinone at pH=5.

NMR Spectroscopy

^{1}H NMR spectra were recorded on Bruker Advance DPX400 (400 MHz) spectrometers. The ^{1}H NMR chemical shifts in deuterated water are reported in ppm relative to tert-butanol (1.24 ppm). Concerning the monitoring of the hydrolysis of PAHc, PAHc was dissolved 0.5 M potassium hydrogenophtalate deuterated solution with DMF as a reference (singlet calibrated at 7.92 ppm)

Electrochemical Quartz Crystal Microbalance (EC-QCM) with Dissipation Monitoring

The electrochemical quartz crystal microbalance (EC-QCM) experiments were performed on a Q-Sense E1 apparatus from Q-Sense AB (Gothenburg, Sweden) by monitoring the changes in the resonance frequency f and the dissipation factor D of an oscillating quartz crystal upon adsorption of a viscoelastic layer. The quartz crystal is excited at its fundamental frequency (5 MHz), and the measurements are performed at the first, third, fifth, and seventh overtones, corresponding to 5, 15, 25, and 35 MHz. The QCM measurement is sensitive to the amount of water associated with the adsorbed molecules and senses the viscoelastic changes in the interfacial material. In the Results section, only the normalized frequency shifts of the fundamental frequency ($\Delta f_1/1$) and the third overtone ($\Delta f_3/3$) are presented. The gold-coated QCM sensor acted as working electrode. A platinum counter electrode on the top wall of the chamber and a no-leak Ag/AgCl reference electrode fixed in the outlet flow channel were used respectively as counter and reference electrodes. Electrochemical measurements were performed on a CHI660E apparatus from CH instrument (Austin, Texas) coupled on the QCM-D apparatus. Before the buildup of the polymer film, in order to test the quality of the EC-QCM cell, a capacitive current and a faradic current of 1 mM of potassium hexacyanoferrate(II) aqueous solution were recorded. A 150 mM $NaNO_3$ aqueous solution was prepared to measure the capacitive current of the EC-QCM cell. 1 mM of potassium hexacyanoferrate(II) was prepared in 150 mM $NaNO_3$ aqueous solution and put into contact with the crystal to monitor its cyclic voltammogram. The polymer film buildup was operated by applying a fixed current (chronopotentiometry in galvanostatic mode).

Film buildup procedure

An anchoring PEI-PSS bilayer was deposited onto the gold working electrode by the LbL technique prior to the polyampholyte film buildup and was monitored by EC-QCM. The aqueous PEI solution (1 mg/ml in 150 mM $NaNO_3$) was injected in the electrochemical cell

(600 µl) at a flow rate of 600 µL/min with a peristaltic pump. Once the signal stabilize, i.e. after ca. 5 min, an aqueous solution of 150 mM $NaNO_3$was injected in the cell to rinse it (600 µl at 600 µl/min) during 2 min. The aqueous polyanion solution (PSS at 1 mg/ml in 150 mM $NaNO_3$) was then injected in the cell (600 µL at 600 µl/min) with the peristaltic pump. Once the signal stabilize, i.e. after ca. 5 min, an aqueous solution of $NaNO_3$ was injected in the cell to rinse it (600 µl at 600 µl/min) during 2 min. An aqueous solution of 150 mM $NaNO_3$ containing PAHc (1 mg/ml) and hydroquinone (60 mM) at pH = 5 was then injected in the electrochemical cell (600 µl at 600 µL/min). Once the signal stabilized, a flow rate of 50 µl/min was established. A galvanostatic current ranging from 50 to 100 µA was then applied to trigger the hydroquinone oxidation and start the polyampholyte film buildup. After a construction time of 1 h, an aqueous solution of 60 mM Hydroquinone in 150 mM $NaNO_3$ was injected in the cell (600 µL at 600 µl/min) while the electrochemical stimulus was still applied in order to maintain the low pH in the vicinity of the electrode. Once the signal stabilizes, i.e. ca. 5-10 min, air was injected in the electrochemical cell while the fixed current was still applied. The absence of reactive species in the cell leads to an increase of the tension from 0.3-0.4 V (oxidation potential of hydroquinone) to 0.7 V, the defined value at which the potentiostat stops. The gold working electrode was then un-mounted from the EC-QCM and dried with a flow of dry air for 5 min and the samples were stored in dry state.

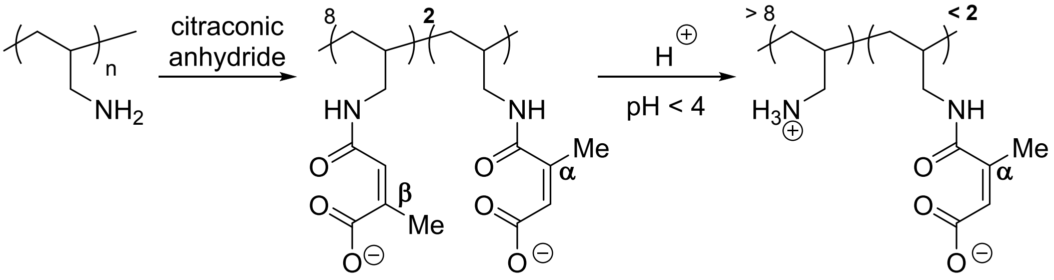
Atomic Force Microscopy

Polyampholyte based films were built on the QCM quartz crystal inside the EC-QCM apparatus. AFM images were obtained in contact mode in dry or liquid state with the Nanoscope IV from Veeco (Santa Barbara, CA). Cantilevers with a spring constant of 0.03 N/m and silicon nitride tip (model MSCTAUHW, Veeco) were used. We always performed several scans over a given surface area. These scans had to produce comparable images to ascertain that there is no sample damage induced by the tip. Deflection and height images (10 µm × 10 µm) were scanned at a fixed scan rate (2 Hz) with a resolution of 512 × 512 pixels.

X-ray photoelectron spectroscopy

The chemical composition of polyampholyte based films was determined by using X-ray photoelectron spectroscopy (XPS). This analysis was performed with a Thermo VG Scientific spectrometer, equipped with an Al K_α X-ray source (1486.6 eV). It operated at 225 W under ultrahigh vacuum (pressure lower than 5.0×10^{-8} mbar). The incident angle and the source to analyzer angle were set to 45° and 90°, respectively. The probing depth of the technique is estimated to range from 5 to 8 nm. The survey scans were collected from 0 to 1100 eV with pass energy of 50 eV and the high resolution scans were performed with the pass energy adjusted to 20 eV. The spectra were recorded by using Avantage V.2.26 software and analyzed with CasaXPS 2.3.16 software. For calibration purposes, the carbon C_{1s} electron bond energy corresponding to aliphatic carbon was referenced to 285.0 eV. Raw areas determined after background subtraction were corrected according to Scofield sensitivity factors (C_{1s}: 1.00; N_{1S}: 1.80; S_{2p}: 1.68). The curve fitting was performed using a convolution of Gaussian and Lorentzian line shapes with a typical ratio of 70:30. This peak-fitting procedure was repeated until an acceptable fit was obtained with consideration of peak position, full width at half-maximum.

Section 1: Kinetic of hydrolysis of PAHc monitored by ^{1}H NMR at various pH



Poly(allylamine) **PAHc** **Partially hydrolyzed PAHc: Polyampholyte**

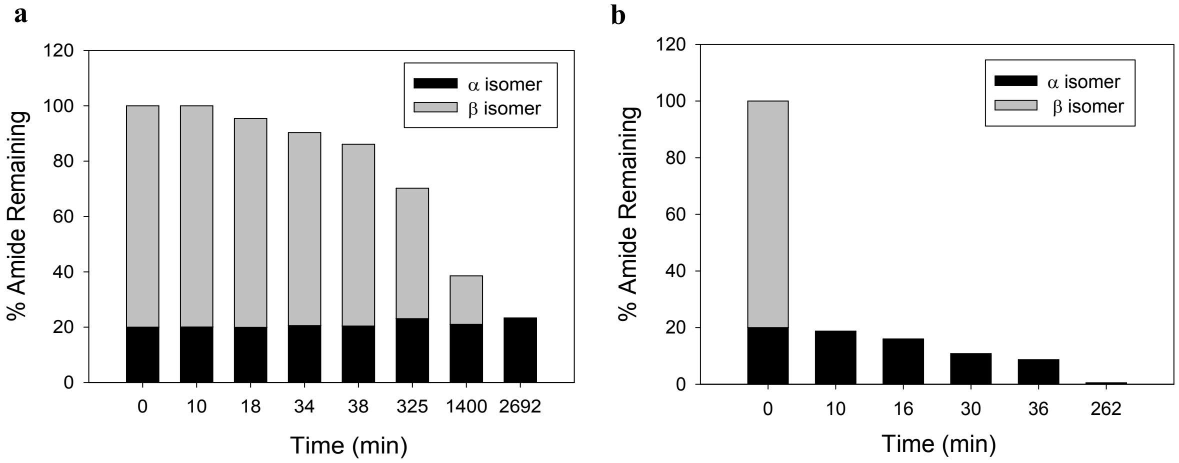


Fig. S1: Relative proportion of α and β isomers of amide remaining on PAHc, monitored by ^{1}H NMR, a function of time in solution at (a) pD 5.89 and (b) pD 4.18.

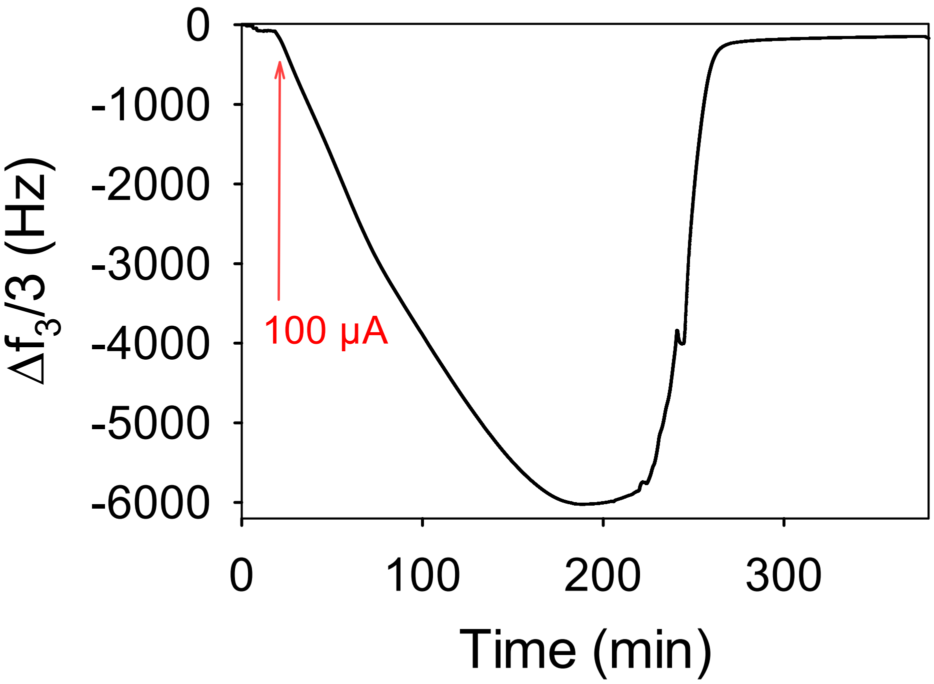


Fig. S2: Evolution of the normalized frequency shift, $\Delta f_3/3$, as a function of time at an applied current of 100 µA of PAHc solution (1 mg/mL) in the presence of 60 mM of hydroquinone in contact with a PEI-PSS pre-coated electrode.

Section 2: XPS analysis

The binding energies and area percentages of nitrogen included-functionalities are gathered in the following table. The polyampholyte film was built from PAHc (1 mg/mL) solution in the presence of 60 mM of hydroquinone by the application of 100 µA for 30, 45 and 60 min. Area measurements corresponding to amino (NH_2), ammonium (NH_3^+) and citraconamide groups (NHCO) are reported for the three films. Experimental set-up is given above in the Material and Methods section of this ESI.

Table S-1 XPS area measurement of the amino (NH_2), ammonium (NH_3^+) and citraconamide groups (NHCO) for polyampholyte films built from PAHc (1 mg/mL) solution in the presence of 60 mM of hydroquinone by the application of 100 µA for 30, 45 and 60 min on a PEI-PSS precoated substrate.

t (min)	**XPS peak area (%)**		
	NH_2 (399.7 eV)	**NHCO** (400.6 eV)	**NH_3^+** (402.0 eV)
30	46	36	17
45	57	27	16
60	57	27	16

Section 3: Crosslinking of polyampholyte-based film through a heat treatment: process and AFM images

Polyampholyte based films were obtained using PAHc solution (1 mg/mL) in the presence of 60 mM of hydroquinone at an applied current of 100 µA for 1 h on a PEI-PSS precoated substrate using the procedure described in Material and methods section in this ESI. At the end of the film buildup, the polyampholyte-coated QCM crystal was placed in an oven at 150°C for 12h. The so-crosslinked film was imaged by AFM in dry condition before immersion in MilliQ water and after contact with 5 mL of MilliQ water for 2h. The sample was then hydrated again in the same conditions in MilliQ water and imaged by AFM in liquid state for the third time.

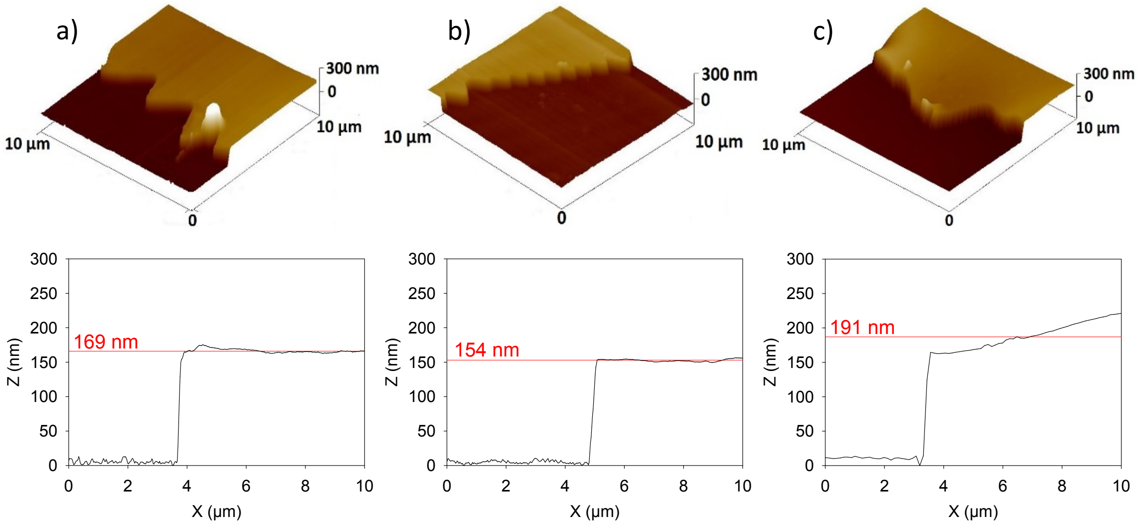


Fig. S3 Polyampholyte based films obtained at an applied current of 100 µA for 1 h and cross-linked by a heat treatment at 150°C for 12 h. (a) AFM image in dry state before immersion in Milli Q water with a mean thickness of 168.7 ± 5.2 nm, (b) AFM image in dry state after immersion in MilliQ water for 2h with a mean thickness of 154.5 ± 1.7 nm and (c) AFM image in liquid state at the second immersion in MilliQ water with a mean thickness of 191 ± 11 nm.