# Electrically Induced Disassembly of Electroactive Multilayer Films Fabricated from Water Soluble Polythiophenes

*Damia Mawad,* Paul J. Molino, Sanjeev Gambhir, Julie M. Locke, David L. Officer, and Gordon G. Wallace**

**A novel approach to induce disassembly of electroactive multilayer films fabricated by the layer by layer assembly technique is reported. Electroactive multilayer films are constructed using water soluble polythiophenes, i.e., negatively charged poly[ammonium (3-thienyl)ethoxypropanesulfonate] (SPT) and positively charged poly[3-(3′-thienyloxy)ethyltriethylammonium] (APT). "Induced" dissolution of the films in response to applied potential is investigated using a quartz crystal microbalance equipped with an electrochemical cell module (EC-QCM-D). Disassembly of the films is observed in response to three different potentials: +650, –650, and ±650 mV; however the time for dissolution varies as a function of the potential with films subject to +650 mV dissolving fully in 19 h compared to 42 h for films subject to –650 mV. These electroactive films and their controlled dissolution under applied potential represent an attractive architectural feature for bionic devices that could benefit from their conductivity and dissolution over time.**

## 1. Introduction

Conducting polymers (CPs) are of growing importance in the medical field with potential applications in tissue engineering,[1] drug delivery,[2] bioactuators,[3] and biosensors.[4] Since attracting interest as suitable matrices in biomedical applications,[5] there have been pioneering efforts to replace the permanent non-degradable CP matrices with a degradable biocompatible material.[6–10] Recently, we have developed a bioerodible conducting platform based on the water soluble CP, poly[ammonium (3-thienyl) ethoxypropanesulfonate] (SPT) and poly(ethyleneimmine) (PEI), assembled by the layer by layer (LBL) technique.[11] We demonstrated that the electroactive SPT-PEI multilayer films fully eroded at physiological pH. Erosion times could be varied from 83 to 130 days by changing assembly parameters such as the number of bilayers or the ionic strength of the polyelectrolyte solutions used. It was established that the polymers were not undergoing any chemical degradation but rather dissociating from the multilayer system and dissolving into the buffer solution over the incubation period. The dissociation of the multilayer polyelectrolyte complexes was attributed to the diffusion of salt ions into the films forcing the polymer/polymer ion pairs apart and leading to film erosion.

The assembly and disassembly of an electronically conducting polyelectrolyte structure in a programmable manner is an attractive architectural feature for bionic devices. The disassembly of LBL films is of interest not only for the design of a controlled drug delivery system, but also as means to erode or degrade the films once their medical function has been fulfilled. To this end, disassembly of LBL films has been extensively investigated and has been reported to be triggered by external stimuli such as ionic strength,[12] pH,[13] hydrolysis,[14] enzymatic[15] or chemical reactions.[16] More recently, the influence of applied electric field on the disassembly of LBL films has been investigated as a new external stimulus.[17–20] For instance, Boulmedais et al.[17] investigated the influence of an electric potential on the behavior of heparin and poly(L-lysine) polyelectrolyte multilayers (PLL-HA) assembled on a conductive ITO substrate. Application of voltages above 1.8 V induced dissolution of the films and by switching the potential on and off, the dissolution process could be controlled. Presumably, the high voltage required to induce dissolution is due to the non-conductive nature of the two polyelectrolytes. Guillaume-Gentil et. al.[19] explained that the dissolution process of PLL-HA is due to water electrolysis at the surface of the ITO where a proton gradient is established causing the disruption of the ionic interaction between the layers. However, dissolution of multilayers by pH driven mechanism would not be appropriate in vivo where electrolysis should be avoided. In a study by DeLongchamp et al.,[21] nanocomposite films assembled from Prussian blue nanoparticles and PEI were shown to dissolve under applied oxidative potentials greater than ~1 V. Additionally, successful release of a model drug could be achieved upon induced dissolution of these films by application of 1.25 V.[22]

Having previously established that SPT-PEI multilayer films promoted cell adhesion and proliferation,[11] we were interested in further exploring CP-based LBL films as erodible functional platforms for biomedical applications. We hypothesised that the dissociation of multilayer films assembled from two

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DOI: 10.1002/adfm.201200999

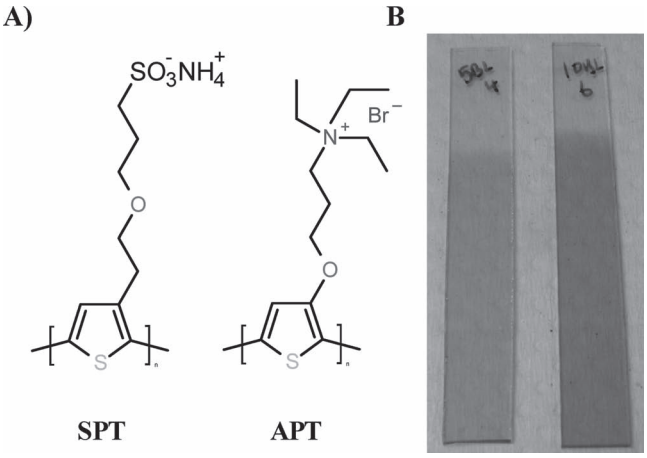


**Figure 1.** A) Chemical structures of SPT and APT. B) APT-SPT 5 and 10BL films.

conducting polymers could be induced by applying a potential to alter the redox state of the polymers that would disrupt the ionic interaction between the layers. This potential could be substantially lower for a conducting polymer than previously required to disassemble non-conducting systems as discussed above.[17,21,22]

The LBL assembly of electroactive multilayers based on water soluble polythiophenes has been previously studied; the properties and structures of the multilayer films have been investigated[23] as well as the effect of the side chain length and the regioregularity of the polyelectrolytes on the film properties.[24,25] However, the stability of these films in response to applied potentials has not been investigated.

Here we report the disassembly of CP-based multilayer films controlled by applied potentials for the first time. Electroactive films were constructed from the negatively charged SPT and the positively charged poly[3-(3′-thienyloxy)ethyltriethylammonium bromide] (APT) (**Figure 1**). "Induced erosion" (disassembly under applied potential) of the multilayer films was monitored using an electrochemical quartz crystal microbalance with dissipation monitoring (EC-QCM-D). QCM-D measures changes in the frequency (ΔF) and dissipation factor (*D*) of an oscillating quartz crystal upon adsorption of polyelectrolytes. A decrease in ΔF denotes a mass uptake, which includes the coupled water with the adsorbed layer.[26] *D* is a measure of energy loss and often an increase in *D* is interpreted as an increase in the viscoelasticity of the film.[26,27] APT-SPT multilayer films were assembled on gold-coated sensor crystals and were used as the working electrode in the QCM-D equipped with an electrochemical cell (EC-QCM-D). Three different potentials were applied and disassembly of the films was recorded in situ. For comparison, "passive erosion" (disassembly without external stimuli) was assessed in PBS as previously described.[11]

## 2. Results and Discussion

### 2.1. Multilayer Films: Polymer Characterization and Film Assembly

APT and SPT were synthesized according to the literature.[23,28] Both polymers were soluble in water at a suitable concentration for multilayer assembly (0.05 wt%). Determining the molecular weight of cationic polythiophenes has been reported to be very difficult[23] and hence it was not attempted in this study. However, UV-vis spectroscopy studies on aqueous solutions of the polymers were carried out to verify the conjugated nature of the polymers. As shown in **Figure 2**, the absorbance maxima of APT

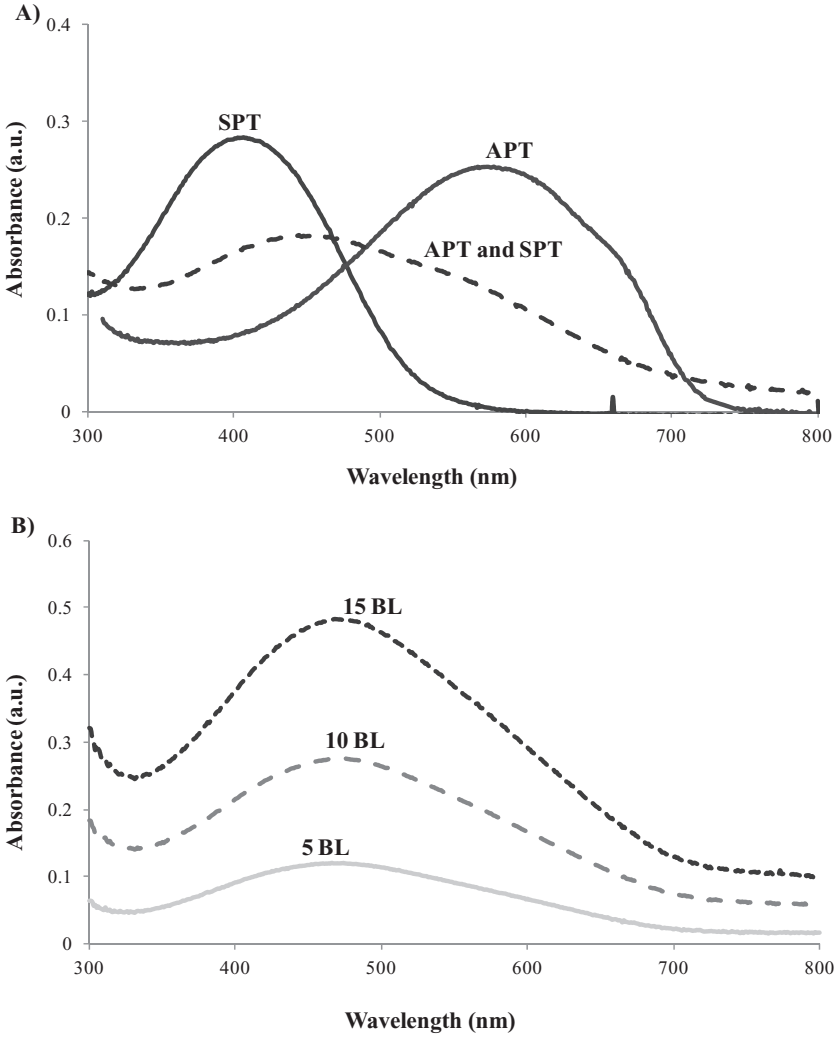


**Figure 2.** A) UV spectra of aqueous solutions of SPT (red), APT (purple), and a 1:1 mixture of APT and SPT (dash brown). B) Electroactive APT-SPT 5 (solid orange), 10 (dash orange), and 15 (dash brown) BL films.

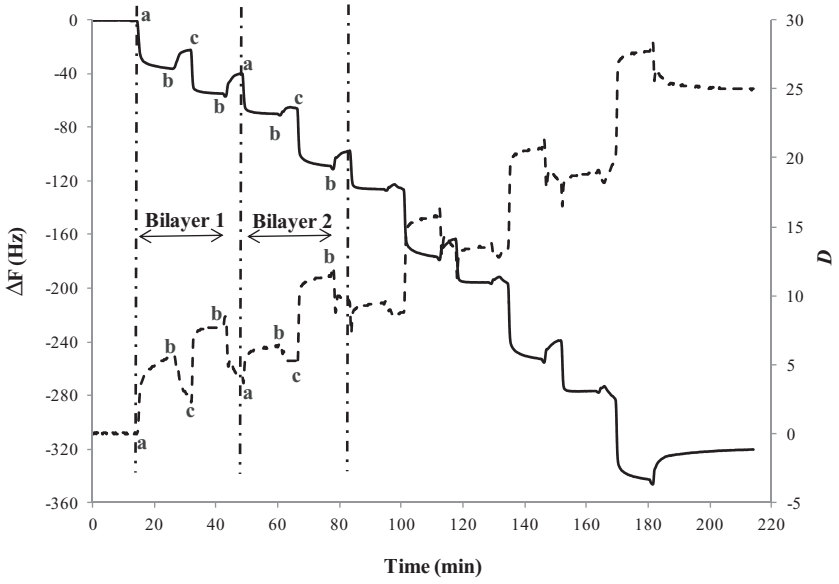


**Figure 3.** Changes in frequency (ΔF; solid line) and dissipation (*D*; dashed line) of the fifth overtone due to adsorption of APT and SPT. The fabrication pattern for the first two bilayers is indicated: a) injection of APT solution followed by 10 min incubation, b) injection of water for rinsing over 5 min, and c) injection of SPT solution followed by 10 min incubation.

and SPT were at 578 nm and 407 nm, respectively, and attributed to the $\pi$–$\pi^*$ transitions of the polymer conjugated systems. The absorbance maximum of APT at longer wavelength indicates a much higher effective conjugation length of the polymer in comparison to other synthesized poly(alkoxythiophenes) that typically exhibit broad adsorption bands between 400 and 500 nm.[25] Interestingly, the 1:1 mixture of SPT and APT in water gave a broad absorbance band at 445 nm that is not simply a superposition of the two individual polymer spectra. This suggests that the two polymers strongly interact with each other in solution.

Electroactive multilayers were formed by the sequential adsorption of APT and SPT. Films up to 15 bilayers (Figure 1B) were successfully fabricated using an automated dip coater. The deposition of APT-SPT 5 bilayer films was monitored in situ using the QCM-D. **Figure 3** represents the frequency shift and dissipation change directly obtained from the QCM-D measurement. The frequency shift (ΔF) decreased after each adsorption step, representative of an increase in mass adsorbed to the QCM sensor electrode surface. As the number of layers increased, SPT induced a higher increase in dissipation (*D*) while after the first two bilayers APT had little effect on *D*. This correlates with the apparent mass deposition of each polymer. As indicated by the frequency change (ΔF), the mass increase on APT addition is constant. In stark contrast, the ΔF and therefore mass change as a result of SPT addition steadily increases. Given that the analogous dissipation becomes proportionally larger than the increase in frequency, this leads us to the conclusion that each subsequent layer of SPT has a higher viscoelasticity or hydration.[29] A likely reason for this is that the more polar nature of the sulfonate group of SPT introduces more water into the film.

The electroactivity of the multilayer films assembled on ITO was investigated using cyclic voltammetry (CV) in 0.1 M PBS (**Figure 4**). The 5 bilayer (5BL) film exhibited an anodic peak at 0.36 V whereas the 10 and 15 bilayer (10 and 15BL) films had a redox peak at 0.45 V with increasing current magnitude. This behaviour might suggest that the more layers assembled, the higher the potential required to oxidise the two polymers and therefore introduce ions into the system. All multilayer films exhibited two broad reduction peaks at 0.71 and 0.42 V. Thus, effective charge transport can occur through the multilayers upon incubation in PBS.

### 2.2. Multilayer Film Disassembly

Dissolution of the multilayer films in response to applied potentials (schematically presented in **Figure 5**a) was assessed and monitored using EC-QCM-D. APT-SPT 5BL films assembled on gold-coated quartz were placed in the electrochemical cell and the electrolyte PBS was injected into the chamber. The temperature was set to 37 °C and the assembled cell was left to equilibrate until the F and *D* stabilized, providing a baseline from which to monitor changes to the adsorbed mass on the QCM electrode surface (i.e., APT-SPT multilayer film).

In order to minimise the potential required to disrupt the bilayers, we investigated the use of potentials (–300 to + 300 mV) up to the onset of oxidation of the bilayer structures

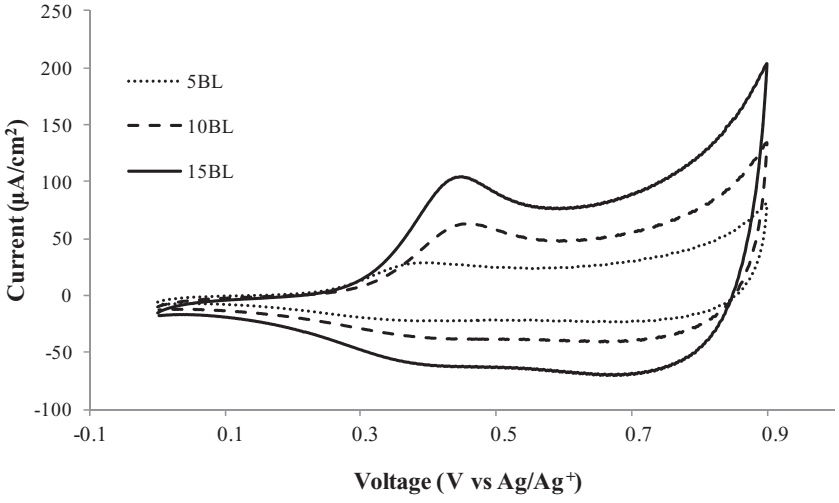


**Figure 4.** Cyclic voltammograms (100 mV/s) of APT-SPT 5, 10, and 15BL films (1 $cm^2$) assembled on ITO in 0.1 M PBS.

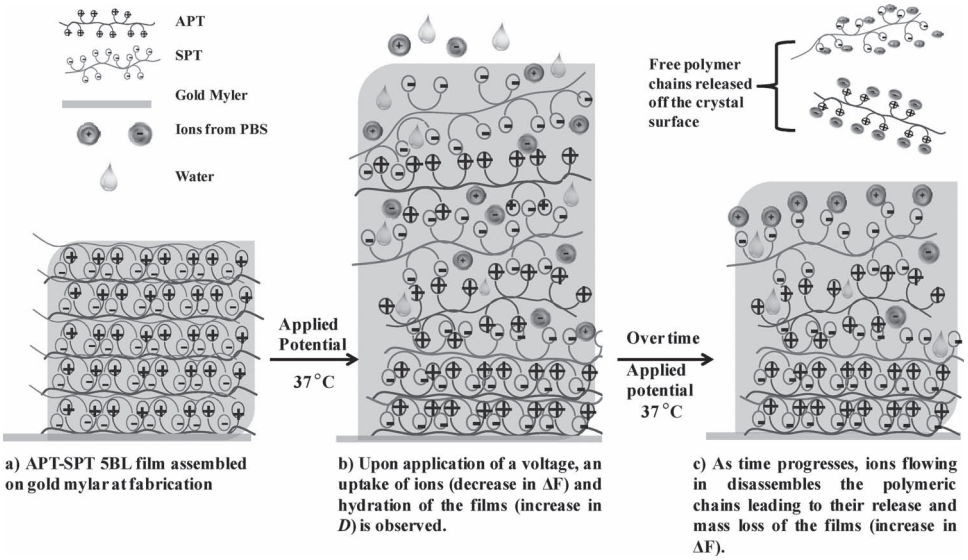


**Figure 5.** Schematic representation of the disassembly process of electroactive multilayer films in response to applied potentials. a) APT-SPT 5BL film assembled on gold mylar and used as the working electrode in the EC-QCM-D disassembly experiment, b) introduction of ions and film hydration on initial application of applied potential, and c) film disassembly over time during applied potential.

(Figure 4). No change in the mass of the films was detected as monitored by the QCM over 3 days. As a result, we chose to apply +650 mV, which is higher than the anodic peak of the bilayer to ensure oxidation of both polymers.

**Figure 6** depicts typical ΔF and *D* profiles obtained from the EC-QCM-D after the application of a constant potential of +650 mV. Three phases could be inferred from the frequency profile. Upon application of the potential, a decrease in frequency (phase 1, Figure 6) is observed over a period of ~4 h. This increase in mass could be attributed to the oxidation of the polymers and concomitant diffusion of ions into the film. During oxidation of a conducting polymer film, ingress of ions from the electrolyte occurs to maintain the electroneutrality of the film,[30] which accounts for the observed increase

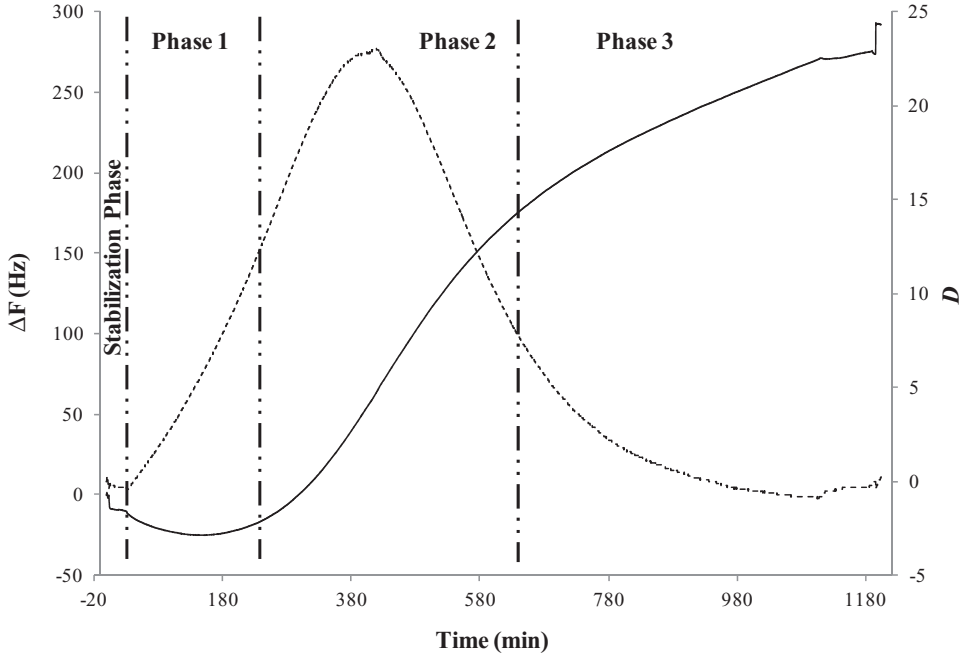


**Figure 6.** Changes in frequency (ΔF; solid line) and dissipation (*D*; dashed line) of the fifth overtone in response to the application of a constant potential of +650 mV on APT-SPT 5BL film.

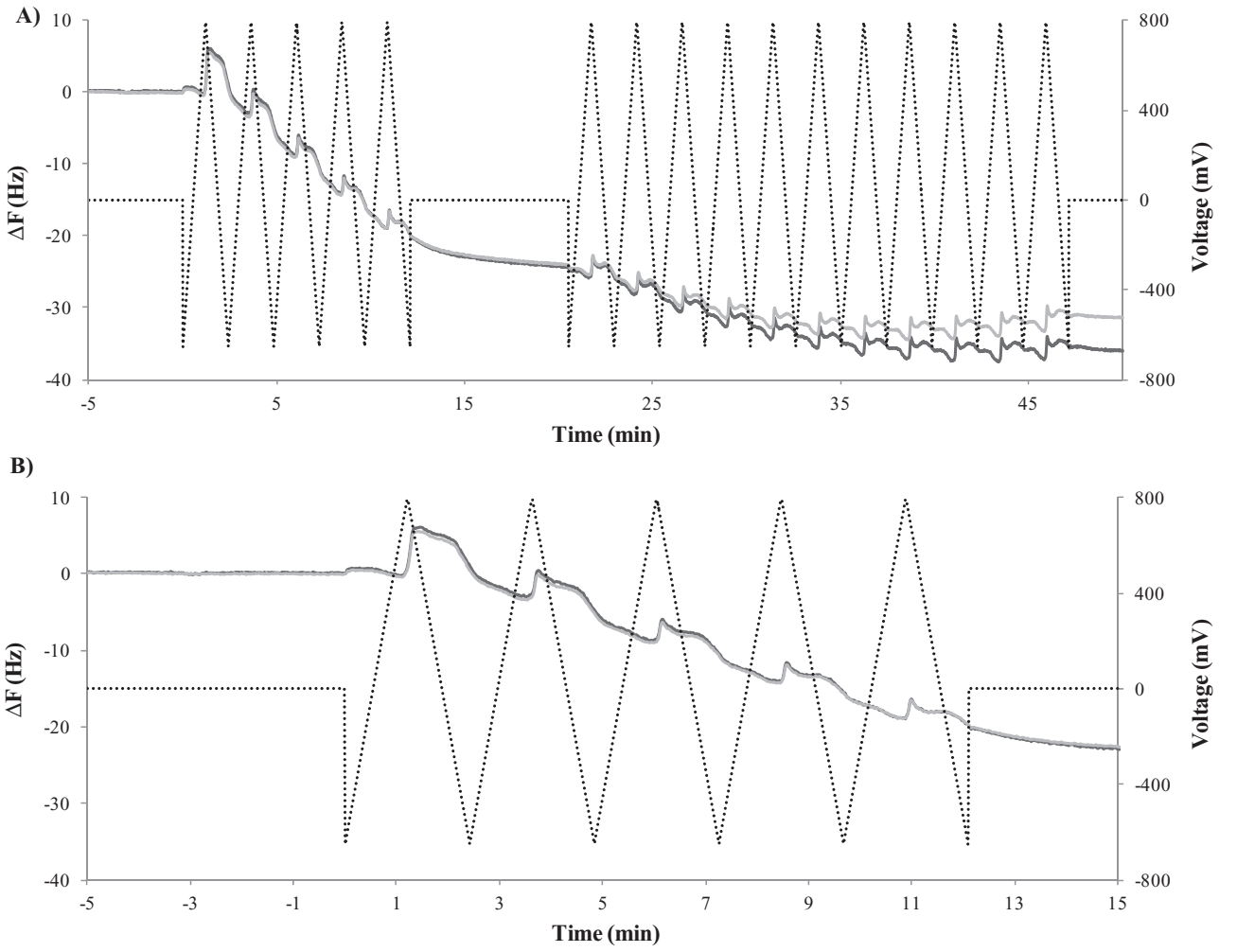


**Figure 7.** Changes in frequency (*f*; solid line) (fifth [red] and seventh [blue] overtones) during CV potential cycling (dotted line) of APT-SPT 5BL film at 20 mV/s. A) 16 cycles with halt in potential after 5 cycles to show the interruption in ion transport in and out of the films. B) The first 5 cycles to help the reader visualize better the ion transport through the films.

in mass (Figure 5b). This leads to a polymer volume increase and a corresponding ingress of electrolyte components. This is supported by the dissipation changes (Figure 6), which reveal unique information about the changes in the viscoelastic properties and morphology of the multilayer film. An immediate and very rapid increase in energy dissipation is observed when the potential of +650 mV is applied (phase 1). This effect is likely due to changes in the viscoelastic properties of the multilayer film as a result of both ion influx into the system as well as hydration from the coupled water.

Thereafter, a reduction in the film mass (phase 2) was detected as an increase in the oscillation frequency. Phase 2 is the core experimental event and occurs over the longest period of time. It is the period over which the film is being disassembled. As time progresses (phase 2, Figure 6), the ions diffusing in the film bind to either the polyanion or polycation polymer disrupting the ionic interaction between the two polyelectrolytes that is responsible for holding the layers together. As a result, the polymeric chains start dissociating from the multilayer system and go into solution (Figure 5c). This phenomenon is reflected in the drop in the mass of the film (positive ΔF).

Monitoring the dissipation, two profiles are observed during phase 2. Once the film starts dissolving, the dissipation continues to increase possibly due to the hydration of the under layers, which might have not been accessible in earlier stages. The dissipation reaches a maximum before it starts decreasing. The decrease in the dissipation profile could be attributed to a slower erosion process as a result of polymer depletion off the surface. Phase 3 is marked with a drop in both the frequency and dissipation variation until a plateau is reached. At this stage, no further changes at the surface of the crystal could be detected suggesting that all the APT-SPT multilayer film had dissolved off the surface.

In order to gain insight into this proposed ion influx mechanism, the frequency shift and dissipation changes were monitored during the application of CV on the APT-SPT 5BL film (**Figure 7**). The film was cycled repeatedly between –650 and 800 mV at 20 mV/s, thus only probing the very early stages of

phase 1 (Figure 6) in which no polymer mass loss occurs. The changes in frequency with CV cycling (Figure 7) show clearly the flux of ions/solvent into the film in response to applied potentials. It can be seen that the frequency change follows the potential changes indicating clear swelling/deswelling of the CP film (Figure 7B). This process is attributed to the flux of ions/water in and out of the film as the state of the polymers is varied between neutral and oxidised (–650 to +800 mV). However, this process is shown to be irreversible denoting that not all the ions taken up by the film are expelled when the applied potential has been varied. Retaining ions inside the films is responsible for the dissociation of the ionic interaction between SPT and APT leading to their release off the surface.

Induced erosion of APT-SPT films was tested in response to three different potential regimes (+650, –650 and ± 650 mV). While the erosion profiles recorded by EC-QCM-D had the same characteristics for the 3 potentials, the rate of mass loss appears to be dependent on the potential applied as illustrated in **Figure 8**. A significant difference between the 3 profiles lies in the onset of phase 2 of the phenomena. Application of a positive potential (+650 mV) resulted in the highest uptake of mass (phase 1, ~4 h) followed by an almost immediate onset of mass loss. This could be attributed to the conductive nature of the film at this potential which allows diffusion of ions[31] throughout the film causing the disruption in the polymer-polymer ionic interactions; thus accounting for the observed complete loss of material at this applied potential. The negative potential of –650 mV lead to a slightly lower uptake of mass that occurs over a similar period of time (phase 1, ~3.5 h); however it could be noted that following phase 1, there was a period of 6 hrs over which the variation in frequency (ΔF) was negligible. For polythiophenes to be n-doped (fully reduced), negative potentials (< –1.2 V) are required;[32,33] thus the multilayer films are in the neutral state at –650 mV and will behave as an insulator between the conductive gold and the electrolyte. Hence, it requires longer period of times for the ions to migrate[31] inside the layers and to eventually cause the disruption needed between the polymer-polymer ionic interaction before a mass loss is observed. Indeed, a sharp increase in mass loss is observed at ~42 h suggesting that enough ions or charge has accumulated in the films causing rapid dissassembly. As expected, the application of the pulsed potential (±650 mV) resulted in a ΔF somewhat intermediate between the two constant potential profiles.

Finally, to verify that the applied potential has a significant role in inducing fast erosion of the films, we incubated APT-SPT 5BL films in PBS at 37 °C and monitored their absorbance according to the protocol we published earlier.[11] **Figure 9** shows %ΔA at $\lambda_{max}$ as measured over time for the 5BL film. Although there is loss of material off the surface as denoted by the drop in absorbance over time, this mass loss is significantly lower than what we observed in the EC-QCM-D experiment as a result of applied potentials. Over a period of 70 days, only 34% of material was lost whereas the time taken for total mass loss of films subject to +650, ± 650

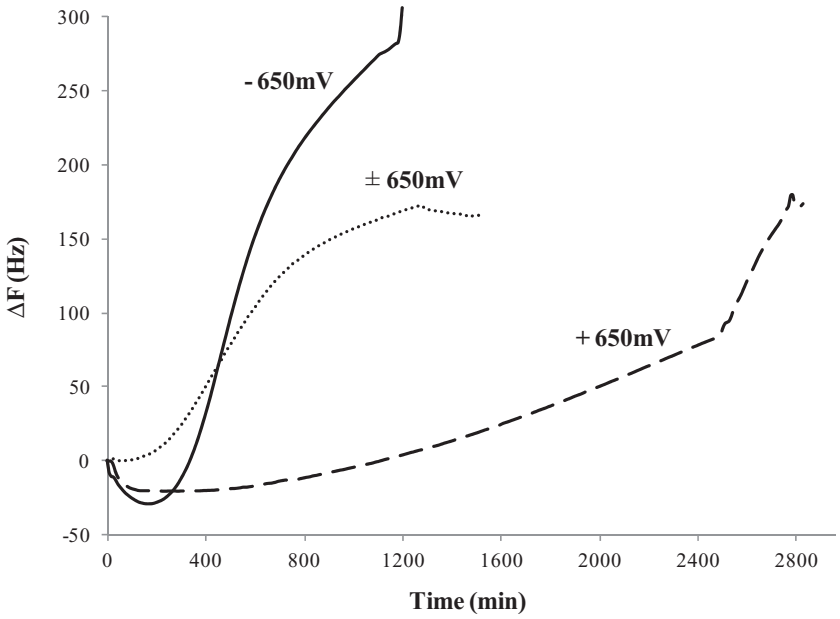


**Figure 8.** Changes in frequency (ΔF) in response to the application of +650 mV (dashed line), ± 650 mV (dotted line), and –650 mV (solid line) on 3 different APT-SPT 5BL samples. The difference in the value of the final frequency change is due to the mass variation observed during the assembly of the multilayer films.

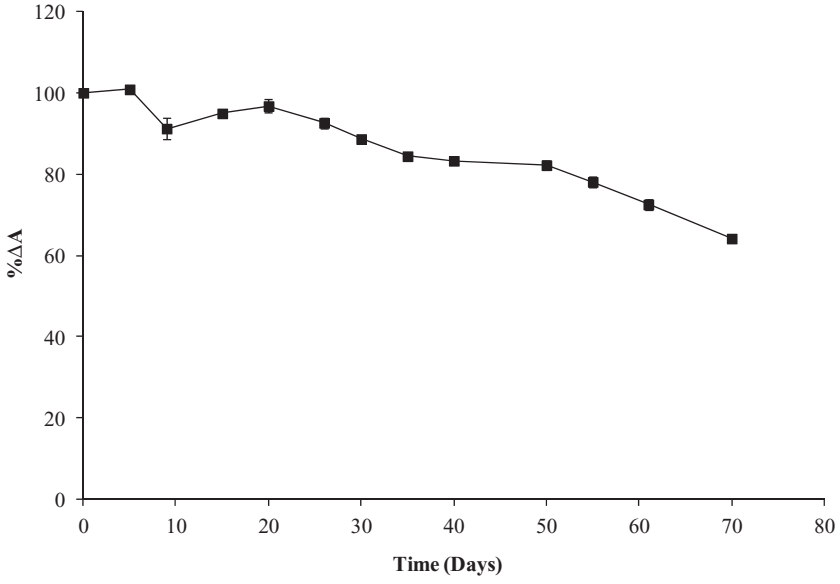


**Figure 9.** % relative change in absorbance for APT-SPT 5BL films undergoing passive erosion. Error bars represent one standard deviation (N = 3).

and –650 mV was 19, 21 and 44 h respectively. This confirms our hypothesis that erosion of CP LBL films could be mediated by changing the redox state of the polymers.

## 3. Conclusions

We have shown for the first time the controlled disassembly of a CP multilayer film constructed from alternating SPT and APT triggered by an external applied potential. Induced erosion of the film, i.e., disassembly under applied potential, was monitored by EC-QCM-D. It was observed that total dissolution of films occurred over a short period of time (19, 21, and 42 h) varying as a function of the applied potential. This is a significant result in comparison to passive dissolution of the films that takes much longer time for complete disassembly. This is the first time that the disassembly of CP-based multilayers has been demonstrated to be induced by the application of potentials, opening the way for new architectural designs for bionic devices.

## 4. Experimental Section

*Materials and General Experimental*: UV-visible spectra of polymers in solution and as films were recorded on a UV-3600 Shimadzu spectrophotometer with the peak maxima in the visible region reported. Multilayer films were fabricated either by using an automated dip coater, KSV Instruments, or quartz crystal microbalance (Q-sense E4, Q-Sense AB, Västra, Frölunda, Sweden). The cyclic voltammetry was recorded using an eDAQ potentiostat system controlled by eDAQ EChem software (v.2.0.7). The counter electrode was a platinum mesh and the reference electrode was an Ag/AgCl in saturated KCl aqueous solution (Bioanalytical System). The working electrode was an ITO coated glass (Delta Technologies Limited) on which the multilayer system was assembled. Electrochemical measurements were performed at 20 or 100 mV/s using 0.1 M PBS electrolyte solutions. In situ erosion of the multilayer films was monitored under applied potentials using Q-Sense Electrochemistry Module, QEM 401.

*Polymer Synthesis and Characterization*: Poly[3-(3′-thienyloxy) ethyltriethylammonium bromide] (APT) and poly[ammonium (3-thienyl) ethoxypropanesulfonate] (SPT) were synthesized as described in the literature[23,28] by chemical oxidation using $FeCl_3$ in dry chloroform. To reduce the synthesised polymers and achieve water solubility, SPT was treated with 10% ammonia solution and APT with aqueous hydroxylamine solution. Polymer solutions were filtered and the filtrates were dried under vacuum to obtain SPT (red in color) and APT (purple in color) dried polymers in their neutral state. Polymers were characterized in the solution state and in the solid state as films by UV-vis spectroscopy. In particular, the absence of absorbances above 750 nm in the UV-vis spectra of APT and SPT solutions confirmed the reduction of the oxidized polymers. The electroactivity of multilayer films was determined in 0.1 M PBS.

*Polyelectrolyte Solutions*: Stock solutions of SPT (0.05 wt%) and APT (0.05 wt%) in 0.2 M NaCl aqueous solution were prepared. All adsorption steps were conducted using these two solutions.

*Multilayer Film Assembly using an Automated Dip Coater*: Multilayer films were fabricated by the layer by layer (LBL) assembly of SPT with APT. Films were either assembled on microscope glass slides (4 × 1 cm) or on indium/tin oxide coated glass (ITO, 1 cm × 1 cm). Prior to the assembly, the slides were washed with ethanol and rinsed thoroughly with DI-$H_2O$. Alternate adsorption of the polymers afforded multilayer growth on the slides. Adsorption times were 10 min for each polyelectrolyte. In between each adsorption step, the slides were rinsed for 2 s with DI-$H_2O$. This procedure was repeated until the desired number of polyelectrolyte layers had been deposited. Films assembled by the dip coater were used for UV characterization, cyclic voltammeter, and passive erosion.

*Multilayer Film Assembly using QCM with Dissipation Monitoring*: QCM-D was used to monitor the assembly of multilayer films on gold coated crystals previously cleaned with Piranha solution. The experiment was started by injecting DI-$H_2O$ to establish a baseline for the frequency (F) and energy dissipation (*D*). APT solution was continuously injected in the chamber for 90 sec then allowed to adsorb for 10 min. The chamber was then rinsed with DI-$H_2O$ continuously injected for 5 min ensuring enough time for the F and *D* to stabilize. SPT solution was then injected over 90 s and allowed to adsorb for 10 min. This process was repeated until 5 bilayer films (5BL) had been prepared. The crystals were removed, rinsed with DI-$H_2O$ and blow dried with $N_2$. Films were stored until their use in the EC-QCM-D experiment.

*Electrochemical QCM with Dissipation Monitoring (EC-QCM-D)*: Induced erosion of APT-SPT 5BL films assembled on gold-coated QCM crystal sensors (as described above) was assessed by Q-sense E4 system along with the electrochemistry module (QEM 401) and a potentiostat. The QCM chamber served as a three-electrode electrochemical cell with a Ag/AgCl reference electrode, a built-in Pt counter electrode, and the gold-coated QCM crystal modified with APT-SPT 5BL film as the working electrode. The electrolyte was 0.1 M PBS solution and the temperature set at 37 °C to emulate physiological conditions. Following the assembly of the chamber, PBS was injected and the system was allowed to stabilize. Cyclic voltammeter was recorded in the range of –650 to 800 mV at a scan rate of 100 mV/s. Then, a constant potential (+650 or –650 mV) or a pulsed potential (± 650 mV) was applied while monitoring changes in F and *D*.

*Passive Erosion of 5BL Films*: to confirm that the applied potentials were inducing erosion of the films over a short period of time, films assembled on glass slides were incubated in PBS at 37 °C and their absorbance monitored at different time points as described previously.[11]

## Acknowledgements

This work was supported by the ARC Centre of Excellence for Electromaterials Science. The authors gratefully acknowledge funding from the Australian Research Council and National Health and Medical Research Council for continued financial support. They would like also to acknowledge the Australian National Fabrication Facility (ANFF) for their support.

Received: April 9, 2012
Revised: June 13, 2012
Published online: July 23, 2012

[1] S. Z. Yow, T. H. Lim, E. K. F. Yim, C. T. Lim, K. W. Leong, *Polymers* **2011**, *3*, 527.
[2] D. Svirskis, J. Trava-Sejdic, A. Rodgers, S. Garg, *J. Controlled Release* **2010**, *146*, 6.
[3] G. M. Spinks, T. E. Campbell, G. G. Wallace, *Smart Mater. Struct.* **2005**, *14*, 406.
[4] L. Xia, Z. Wei, M. Wan, *J. Colloid Interface Sci.* **2010**, *341*, 1.
[5] R. Ravichandran, S. Sundarrajan, J. R. Venugopal, S. Mukherjee, S. Ramakrishna, *J. R. Soc. Interface* **2010**, *7*, S559.
[6] T. J. Rivers, T. W. Hudson, C. E. Schmidt, *Adv. Funct. Mater.* **2002**, *12*, 33.
[7] N. K. E. Guimard, J. L. Sessler, C. E. Schmidt, *Macromolecules* **2009**, *42*, 502.
[8] J. Hu, L. Huang, X. Zhuang, P. Zhang, L. Lang, X. Chen, Y. Wei, X. Jing, *Biomacromolecules* **2008**, *9*, 2637.
[9] L. Huang, X. Zhuang, J. Hu, L. Lang, P. Zhang, Y. Wang, Y. Wei, X. Jing, *Biomacromolecules* **2008**, *9*, 850.

[10] A. N. Zelikin, D. M. Lynn, J. Farhadi, I. Martin, V. Shastri, R. Langer, *Angew. Chem.* **2002**, *114*, 149.
[11] D. Mawad, K. Gilmore, P. Molino, K. Wagner, P. Wagner, D. L. Officer, G. G. Wallace, *J. Mater. Chem.* **2011**, *21*, 5555.
[12] S. T. Dubas, J. B. Schlenoff, *Macromolecules* **2001**, *34*, 3736.
[13] X. Liu, J. Zhang, D. M. Lynn, *Soft Matter* **2008**, *4*, 1688.
[14] R. C. Smith, A. Leung, B.-S. Kim, P. T. Hammond, *Chem. Mater.* **2009**, *21*, 1108.
[15] M. Westwood, D. Roberts, R. Parker, *Carbohyd. Polym.* **2011**, *84*, 960.
[16] A. N. Zelikin, J. F. Quinn, F. Caruso, *Biomacromolecules* **2006**, *7*, 27.
[17] F. Boulmedais, C. S. Tang, B. Keller, J. Vörös, *Adv. Funct. Mater.* **2006**, *16*, 63.
[18] K. Sato, D. Kodama, Y. Naka, J. I. Anzai, *Biomacromolecules* **2006**, *7*, 3302.
[19] O. Guillaume-Gentil, N. Graf, F. Boulmedais, P. Schaaf, J. Vörös, T. Zambelli, *Soft Matter* **2010**, *6*, 4246.
[20] I. C. Kwon, Y. H. Bae, S. W. Kim, *J. Controlled Release* **1994**, *30*, 155.
[21] D. M. DeLongchamp, P. T. Hammond, *Adv. Funct. Mater.* **2004**, *14*, 224.
[22] K. C. Wood, N. S. Zacharia, D. J. Schmidt, S. N. Wrightman, B. J. Andaya, P. T. Hammond, *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 2280.
[23] J. Lukkari, M. Salomaki, A. Viinikanoja, T. Aaritalo, J. Paukkunen, N. Kocharova, J. Kankare, *J. Am. Chem. Soc.* **2001**, *123*, 6083.
[24] J. Lukkari, M. Salomaki, A. Viinikanoja, T. Aaritalo, K. Loikas, T. Laiho, J. Kankare, *Langmuir* **2002**, *18*, 8496.
[25] A. Viinikanoja, S. Areva, N. Kocharova, T. Aaritalo, M. Vuorinen, A. Savunen, J. Kankare, J. Lukkari, *Langmuir* **2006**, *22*, 6078.
[26] D. Grieshaber, R. MacKenzie, J. Voros, E. Reimhult, *Sensors* **2008**, *8*, 1400.
[27] D. Grieshaber, J. Voros, T. Zambelli, V. Ball, P. Schaaf, J. C Voegel, F. Boulmedais, *Langmuir* **2008**, *24*, 13668.
[28] F. Tran-Van, M. Carrier, C. Chevrot, *Synth. Met.* **2004**, *142*, 251.
[29] F. Hook, J. Voros, M. Rodahl, R. Kurrat, P. Boni, J. J. Ramsden, M. Textor, N. D. Spencer, P. Tengvall, J. Gold, B. Kasemo, *Colloids Surf. B* **2002**, *24*, 155.
[30] D. E. Grumelli, F. Garay, C. A. Barbero, E. J. Calvo, *J. Phys. Chem. B* **2006**, *110*, 15345.
[31] X. Wang, E. Smela, *J. Phys. Chem. C* **2009**, *113*, 369.
[32] H. J. Ahonen, J. Lukkari, J. Kankare, *Macromolecules* **2000**, *33*, 6787.
[33] R. Borjast, D. A. Buttry, *Chem. Mater.* **1991**, *3*, 872.