

## Application Note # 136

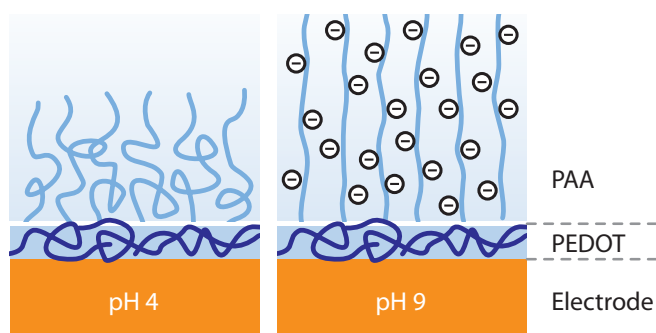
# Polymer collapse and extension monitored with MP-SPR

Multi-Parametric Surface Plasmon resonance (MP-SPR) was utilized to follow poly (acrylic acid) (PAA) polymer brushes swelling and collapse caused by pH or electric potential change. In acidic environment PAA brushes collapsed resulting decrease in polymer thickness. Electric potential change seemed to cause PAA brushes conformational collapse also in basic environment due to conductive polymer (CP) oxidation.

## Introduction

Conductive polymers (CP) are utilized in drug delivery systems, microelectronics, photonics and also for material in biomedical engineering. CP polymer poly (3,4-ethylenedioxythiophene) (PEDOT) have been interesting for biomedical applications due to its established biocompatibility and electroactivity in aqueous solutions. Poly (acrylic acid) (PAA) brushes are well known to be pH responsive. PAA is a promising biointerface material providing sites for bioconjugation and reducing nonspecific interactions with protein in its extended negatively charged state.

MP-SPR is real time optical measuring technique, where changes in refractive index on the sensor surface cause change in the SPR resonant angle. MP-SPR with electrochemical cell can be utilized to form potential change when the sensor surface is conductive. Multi wavelength MP-SPR measures whole SPR curve with two different wavelengths and this can be utilized to calculate deposited layer thickness (more detailed see separate application note).



**Figure 1.** Polymer layers conformational changes in different pH. PAA= poly (acrylic acid), PEDOT= poly (3,4-ethylenedioxythiophene).

## Materials and methods

The CP polymer was deposited by synthesizing (3,4-ethylenedioxythiophene) methyl2-bromopropanoate (BrEDOT) and polymerizing it using cyclic voltametry. PAA brushes were grafted on the electropolymerized PBrEDOT surface by surface initiated atom transfer radical polymerization (ATRP). Pure PBrEDOT was used as a control surface in the experiments. For more details, please see the original publication [1].

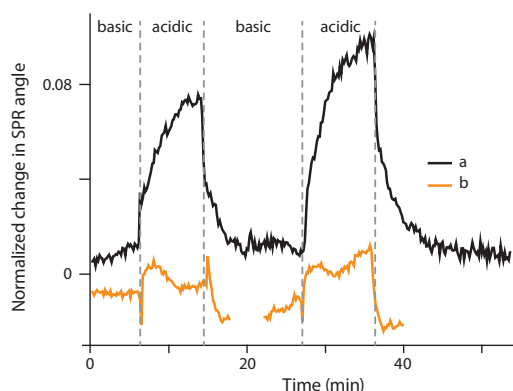
SPR Navi 200-L with microfluidic flow cell was utilized to expose films to acidic and basic liquids (unbuffered MilliQ water adjusted to pH4 or 10) and monitor changes in the surface due to altered pH.

An electrochemical cell was utilized for monitoring changes in film morphology caused by changed potential (0.4, 0 and -0.25 V). Surfaces were measured in 50mM NaCl solution in acidic and basic pH (4 and 9).

## Results and discussion

Optical modelling of the SPR full angular spectra revealed that on the sensor slide had a 18 nm thick PBrEDOT layer and a 15 nm thick PAA layer on top of that.

PBrEDOT-g-PAA revealed to be pH sensitive as expected. In acidic environment (pH4) PAA polymer brushes collapsed resulting a decrease in thickness of the layer and an increase in refractive index of brushes (Fig.2).



**Figure 2.** Change in resonant angle over time when pH of water flow is changed from basic pH (10) to acidic pH (4). a) PBrEDOT-g-PAA and b) PBrEDOT (reference channel)

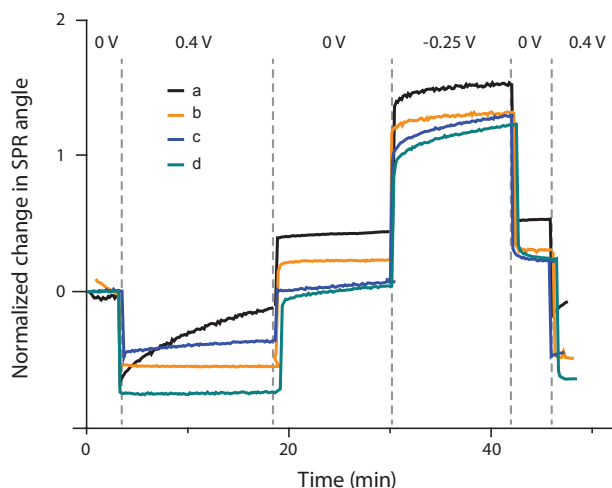
Conducting polymer (CP) film showed a large response to the potential change due to changed oxidation state and thereby refractive index (Fig.3 c-d). In basic environment (pH9) PBrEDOT-g-PAA brushes showed slow increase in SPR resonant angle (Fig.3 a), which was probably caused by PAA brushes conformational collapse during polymer oxidation. In acidic environment (pH4) PAA brushes were already collapsed so similar effect was not detected (Fig.3 b).

## Conclusions

MP-SPR was successfully used to follow polymer conformational changes. Polymer collapsing and extension due to pH or potential change caused clear change in the SPR resonant angle. The SPR Navi™ with electrochemical cell was effective tool to form electric potential change in the surface. This kind of applications can be utilized in wide range of research areas like polymer science, drug delivery and material sciences.

## References:

[1] Malmström et.al., *Macromolecules*, 2013, 46 (12), pp 4955–4965



**Figure 3.** Change in resonant angle over time when potential is changed a) PBrEDOT-g-PAA at pH 9, b) PBrEDOT-g-PAA at pH 4, c) PBrEDOT at pH 9 and d) PBrEDOT at pH 4. Data is normalized to compensate difference in films thicknesses.

### Recommended instrumentation for reference assay experiments

SPR Navi™ 200, 210A or 220A with additional wavelength (L)

Electrochemical cuvette (for electric potential change measurement)

Standard PDMS flow-cell (for pH change measurement)

Sensor surfaces: Au or other metal

Software: SPR Navi™ Control, SPR Navi™ DataViewer, SPR Navi™ LayerSolver