Overview

Characterization of polymer-based systems

Analyse layer build-up, conformation and molecular interaction with QSense QCM-D

Polymer-based systems such as polymer brushes and polyelectrolyte multilayers (PEM:s) are used in many applications where there is a need to tailor the interfacial properties and to promote a certain interaction with the surrounding environment. Desirable properties could be for example biocompatibility, protein repellency, antifouling properties and drug delivery capabilities.

To tailor the interfacial properties of these polymer-based systems, it is important to understand the layer build-up and growth modes, as well as the layer conformation and changes thereof. An additional parameter, influencing the interfacial properties, is the layer hydration.

In this overview, we present how the properties and dynamic behavior of polymer-based systems can be analyzed with QSense® QCM-D, and what information these measurements offer.

The overview covers analysis of:

1. Grafting kinetics of polymer chains
2. Build-up of PEM:s
3. Conformational changes of polymer layers
4. Molecular interaction with polymer layers

Get the full picture of your polymer-based systems

QCM-D is a surface sensitive technology which has been used to analyze polymer-based systems for almost two decades [1, 2]. Via time-resolved information on mass, thickness and viscoelastic properties of surface adhering layers, the method can monitor polymer layer buildup, layer conformation, conformational changes such as transition between hydrated and dehydrated states, as well as molecular interaction with the polymer layers. Running QCM-D analysis at relevant conditions, varying for example surface (substrate) material, temperature, pH, salt concentration or salt type, the properties and dynamic behavior of the polymer-based system can be characterized as well as tailored for a target application.

Analyze layer build-up, interaction, and structural change

Since QCM-D senses hydrated mass, i.e. the mass of both the polymer molecules and the coupled solvent, it is an excellent technology to analyze polymer-based systems where the layer conformation and degree of hydration are important aspects to obtain the targeted interfacial properties. Monitoring the hydrated mass enables not only detection of layer build-up and molecular interaction with the polymer layer, but it also enables analysis of dynamic behavior such the transition between hydrated and dehydrated states, i.e. water uptake and release, which are sensed as changes in mass.

Here we show examples of what typical QCM-D data could look like in the different scenarios. We also discuss what information you could extract from the respective measurement and what questions you could typically answer.

QSense QCM-D is a surface - sensitive real-time technology for label free analysis of surface interactions and reactions. Monitoring changes in resonance frequency, *f*, and dissipation, *D*, of a quartz crystal, surface interaction events can be characterized and quantified.

What you can do: Analyze molecular interactions with surfaces and molecules, time - resolved and label-free.

1. Grafting kinetics of polymer-chains

During the grafting process, the polymer chains can adopt several different conformations depending the interaction between neighboring polymer chains and the interactionss with the surface.

QCM-D monitors mass changes as a function of time and enables analysis of molecular adsorption (desorption) and binding to the sensor surface, which shows as a mass increase (loss) in the QCM-D data, Fig 1. Via the time-resolved information, it is possible to follow grafting kinetics of polymer chains to the surface. The data reveals how fast the process is and what conformation the grafted chains take. The latter is possible since QCM-D also senses the mechanical properties of the surface-adhering layer, i.e. if it is soft or rigid, which in combination with the mass reveals the conformation such as pancake, mushroom or brush. Eliminating time from the data, and plot ΔD vs Δf, i.e. softness vs. mass, the different phases in the grafting process can be revealed, Fig 1d.

Use QCM-D for example to:

- Explore the grafting kinetics as a function of polymer properties and solvent conditions
- Explore whether polymer chain conformation is the same throughout the entire adsorption phase or if the structural arrangement depends on surface coverage.
- Identify the different phases in the polymer grafting process.
- Assess the conformation pancake, mushroom or brush

How to interpret the data

Frequency changes: The frequency, *f*, provides information about mass changes at the surface. A decrease in ***f*** indicates a mass uptake and vice versa

Dissipation changes: The dissipation, *D*, provides information about the layer softness. As a rule of thumb, the higher the *D*, the softer and/or thicker the layer

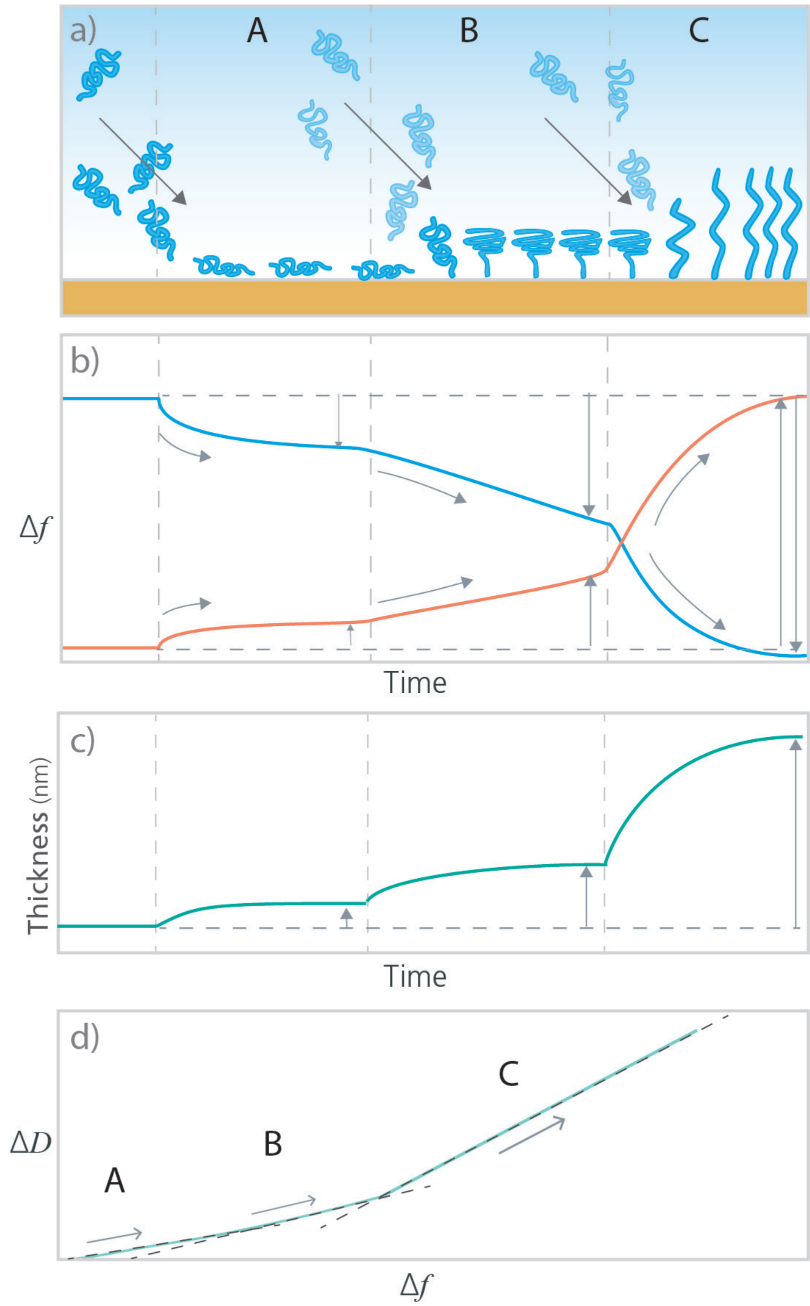


Figure 1. a) Schematic illustration of polymer chains being grafted to a surface. b) The grafting process is characterized by QSense QCM-D, where the Δf (blue) and ΔD (red) data reflect mass change and layer softness respectively. As indicated by the grey arrows, the time-resolved data makes it possible to follow the adsorption/binding process, how fast it is, and how much material that is added to the surface. The data shows in (A) that there is little mass increase and that the layer formed is fairly rigid, which indicates pancake formation. In (B) both the mass and the energy loss increase slowly, which indicates that the layer is reorganizing while coupling more water and that the layer becomes softer, i.e. mushroom formation. In (C), there is a rapid increase in both mass and energy loss, which indicates that the film now couples lots of water and is very soft. This indicates that the polymer chains stretch out from the surface and form a brush. c) Using the data in b), the amount adsorbed to the surface can also be analyzed via quantification of the time-resolved layer thickness or layer mass (not shown). d) The ΔD vs Δf plot reveals whether it is a single- or multi-phase process. In the scenario here illustrated, there are three different slopes, indicating that it is a three step-process.

2. Build-up of PEM:s

Polyelectrolyte multilayers are created by a layer by layer deposition, alternating oppositely charged polyelectrolytes, on to a solid surface.

QCM-D can monitor the PEM growth process in a time - resolved manner. Layer by layer, the build-up process can be measured and changes of the layer thickness, as well as the mechanical properties of the layer, can be characterized, Fig. 2. The multilayer growth mode and the thickness increase throughout the build-up process, for example if it is linear or exponential one, can be assessed. How the growth is influenced by variations in conditions such as the polyelectrolyte structure and the external conditions such as pH, temperature, salt concentration can also be characterized.

Use QCM-D for example to:

- Characterize how different conditions such as chain flexibility, temperature, pH and salt concentration affect the PEM build-up
- Investigate how the PEM thickness increases with layer number
- Assess the PEM stability over time
- Assess PEM degradation

Use QCM-D to analyze processes and properties

- Adsorption, desorption, binding-rates and amounts
- Layer conformation and conformational changes
- Mechanical properties of the layer (i.e. rigid or soft)
- Hydrodynamic thickness

Vary meaurement conditions such as

- Substrate/Surface material
- Temperature
- Solvent
- pH
- Salt concentration
- Salt type

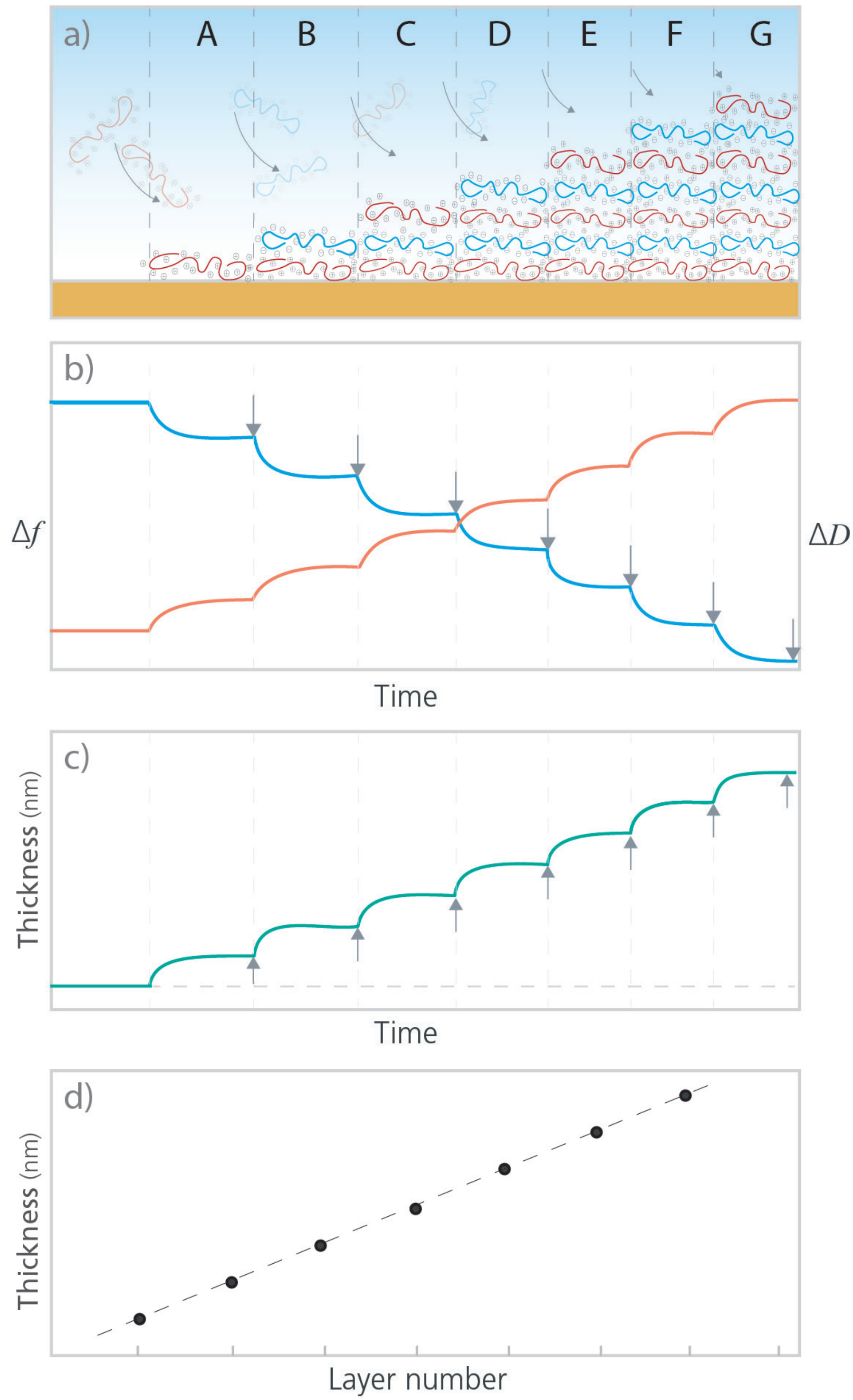
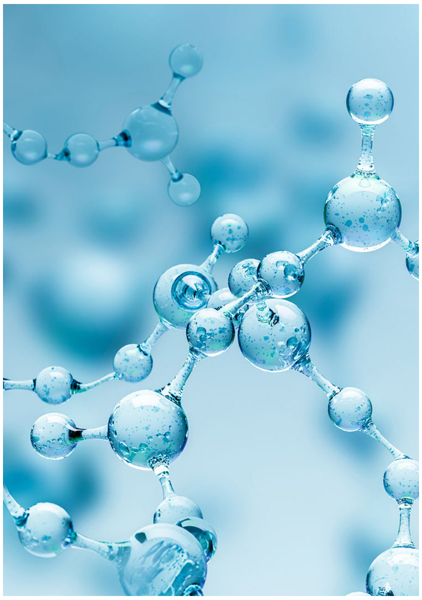


Figure 2. a) Schematic illustration of a PEM build-up process, where a layer is added in each step A-G.
b) The PEM build-up is characterized by QSense QCM-D, where Δf (blue) corresponds to mass changes at the surface and ΔD (red) corresponds to layer softness. As indicated by the grey arrows, the time-resolved data makes it possible to follow the adsorption/binding process, how fast it is, and how much material that is added to the surface. The data shows that for each layer, there is mass added (decrease in Δf) and the layer gets softer/thicker (increase in ΔD).
c) The quantified thickness of the PEM as a function of time.
d) The thickness plotted as a function of layer number shows that the growth process is linear.

Biolin Scientific
[Progress Together]



3. Conformational changes of polymer layers

The ability to control conformation, conformational transition, and the stimuli-responsive properties of the polymer layer is key for the applicability of the material.

As QCM-D senses hydrated mass, i.e. mass including coupled solvent, it is an excellent tool to analyze the structure and structural changes of polymer layers where the transition between hydrated and dehydrated states (i.e. water uptake and release) of for example polymer brush layers, are sensed as changes in mass, Fig 3. As was discussed in section 1, it is possible to asses the conformation during layer build-up. It is also possible to analyze changes, such as swelling and collapse, induced by altered ambient conditions such as temperature and, pH and salt concentration.

Use QCM-D for example to:

- Assess layer hydration and conformation
- Study transitions, swelling an collapse
- Assess conformational changes and stimuli-responsive properties such thermo-responsive properties, pH induced conformational change or solvency-induced conformational change
- Quantify hydrodynamic thickness
- Optimize the conditions to obtain the desired conformation

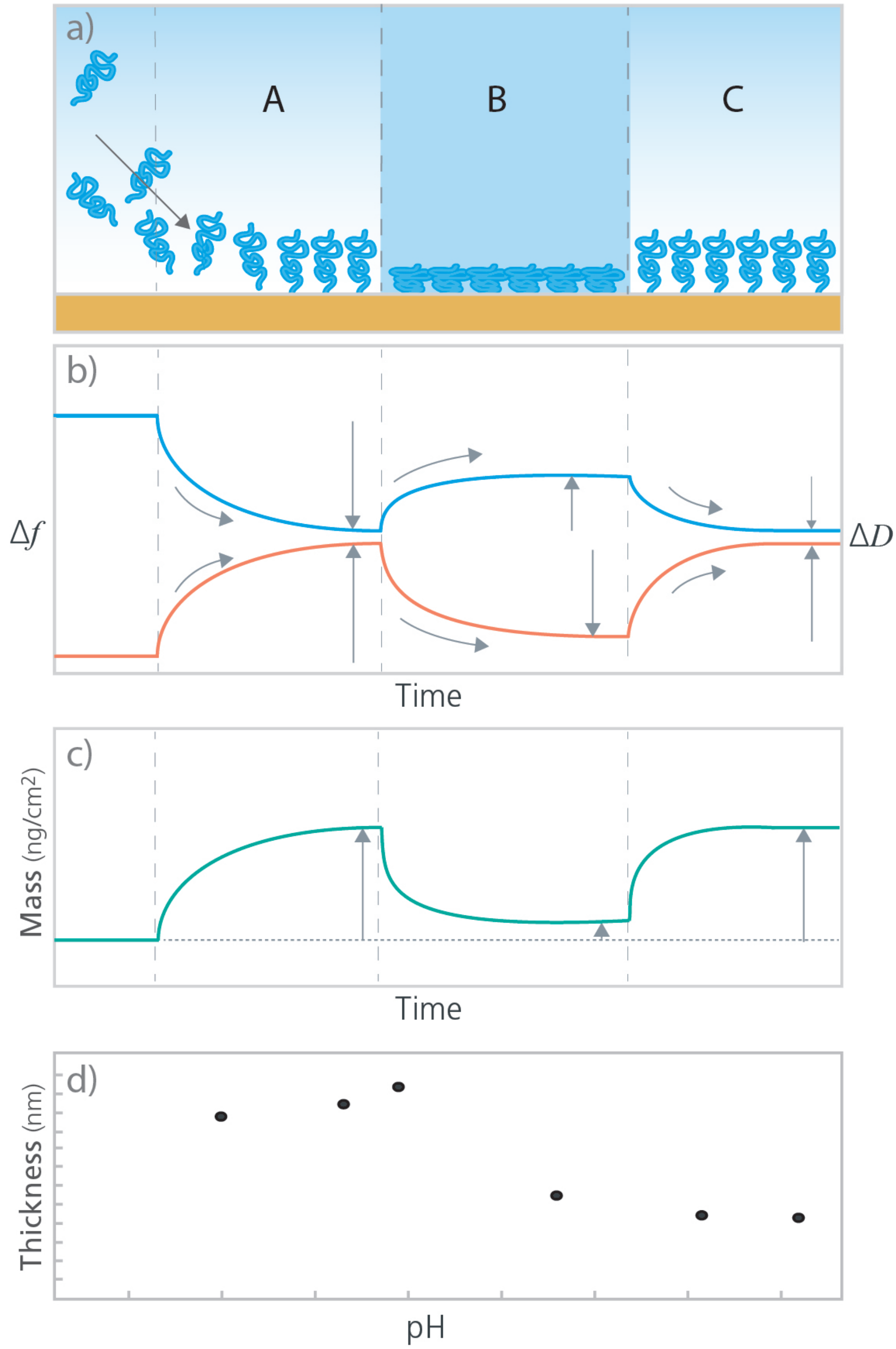


Figure 3. a) Schematic illustration of A) the grafting followed by B) conformational change due to changes in external conditions and C) which are reversible when the conditions are changed back to the original setting. b) The layer grafting and conformational changes are characterized by QSense QCM-D, where Δf (blue) corresponds to mass changes at the surface and ΔD (red) corresponds to layer softness. As indicated by the grey arrows, the time-resolved data makes it possible to follow the adsorption and desorption processes, how fast they are, and how much material that is added to, or lost from, the surface. The data shows (A) the layer build-up and (B-C) that the conformation can be altered in a reversible manner via changes in the ambient conditions. c) The quantified mass as a function of time reveals (B) the layer collapse where mass is lost due to less couple solvent, and (C) layer swelling where mass increase due to increased amount of coupled solvent. d) The thickness plotted as a function of variations in external conditions, here pH.

4. Interaction of molecules with polymer layers

The ambition with polymer - based systems, could be that they should promote a defined interaction with the surrounding. Desired functionality could be for example, biocompatibility, protein repellency, or to promote targeted binding.

QCM-D senses molecular adsorption and binding as changes in mass, and offers a straightforward way to assess molecular interaction, or lack thereof, with polymer layers. As shown in Fig 4, exposing the polymer layer to the molecules to be investigated, the QCM-D result will reveal the molecular interaction with the polymer layer, including the interaction dynamics and the bound amount. The information can be used to verify the desired molecular interaction with the polymer layer, for example to reveal whether a protein binds or not.

Use QCM-D for example to:

- Assess whether the molecule of interest adsorbs/ binds to the polymer layer or not
- Explore the molecular interaction dynamics
- Quantify the adsorption (binding) rate and total adsorbed (bound) amount
- Optimize the polymer layer or solvent conditions to minimize (or maximize) the molecular interaction.
- Identify conditions that prevent molecular interaction

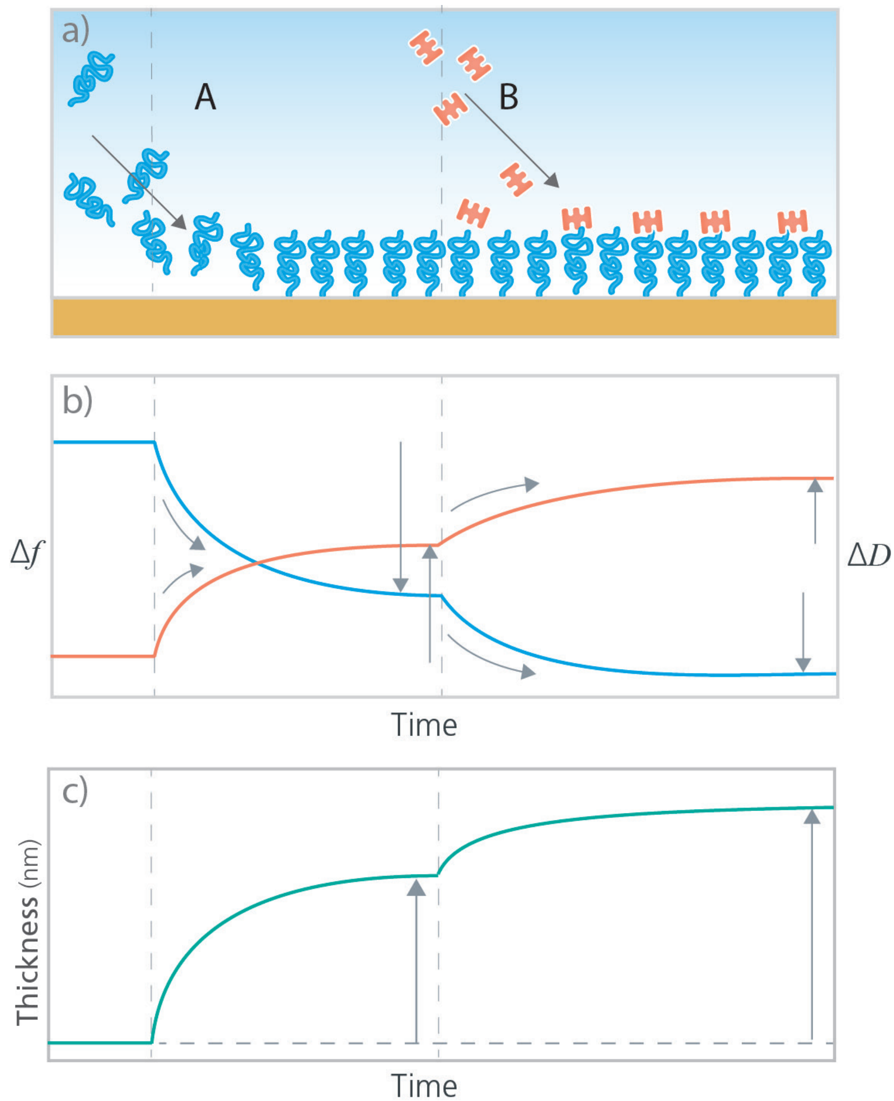


Figure 4. a) Schematic illustration of (A) polymer layer build-up, followed by (B) exposure to molecules.
b) The layer build-up and molecular exposure is characterized by QSense QCM-D, where Δf (blue) corresponds to mass changes at the surface and ΔD (red) corresponds to layer softness. The data shows (A) the layer build-up, followed by (B) molecular adsorption to the polymer layer.
c) The quantified thickness of the polymer layer and the added molecular layer.

In summary, analyze polymer-based systems with QSense QCM-D

- Investigate polymer grafting kinetics
- Asses conformation of end-grafted polymer chains as a function of ambient solvent conditions
- Characterize the build-up and growth process of PEMs
- Assess the layer thickness
- Explore layer responsiveness and stimuli-responsive behavior as a function of changes in the external conditions, such as pH, temperature and salt concentration
- Characterize molecular interaction with polymer layers, such as binding, protein repellency and antifouling properties

References

1. F. Höök, et al., The Dissipative QCM-D Technique: Interfacial Phenomena and Sensor Applications for Proteins, Biomembranes, Living Cells and Polymers, 1999 Joint Meeting EFTF - IEEE IFCS, Volume 2, 1999, pp:966 - 972 vol.2
2. G. Liu and G. Zhang, QCM-D studies on polymer behavior at interfaces, Springer, 2013

Contact us at info@biolinscientific.com

Biolin Scientific
[Progress Together]