Salt- and pH-Induced Swelling of a Poly(Acrylic Acid) Brush via Quartz Crystal Microbalance w/ Dissipation (QCM-D)

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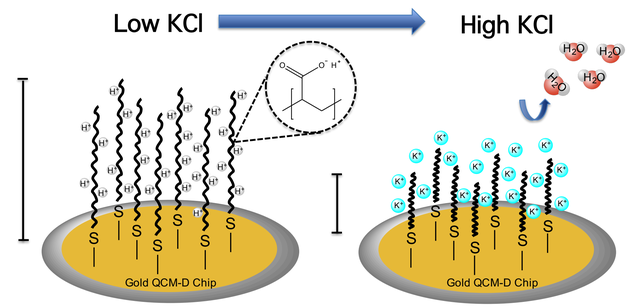
Introduction

- **Polyelectrolyte brushes (PEBs)** are desirable for their swelling behavior in aqueous conditions for use in water harvesting, colloidal stabilization, and lubrication
- PEBs are also ideal model systems for studying polyelectrolyte multilayers (aka **layer-by-layer (LbL)** films), which are used in a variety of fields including drug delivery
- **Weak PEBs** are modifiable as their charge density and resultant swelling behavior is altered by the pH which affects the extent of chain ionization
- **Quartz Crystal Microbalance w/ Dissipation (QCM-D)** can be used to measure subtle changes in adsorbed mass and material viscoelasticity
- The swelling/de-swelling behavior of a weak PEB of **Poly(acrylic acid) (PAA)** self-assembled on a gold crystal was investigated using QCM-D to investigate the effect of **salt concentration, pH,** and **grafting density** on the resultant swelling behavior with comparison to scaling predictions from established **self-consistent field theory (SCFT),** which predicts various characteristic regimes.



Osmotic Brush (OB) Regime Salted Brush (SB) Regime

Method

- In QCM-D, the **change in frequency (ΔF)** corresponds to a **change in finite mass (Δm)** (Sauerbrey relation) & **change in dissipation (ΔD)** is a measure of rigidity as described below.
  Note: The dry thickness & bulk solvent (density ΔF & rigidity ΔD) must also be considered to calculate the brush thickness.

$$\Delta F = -\Delta m\left(\frac{2f_0^2}{\sqrt{\mu_q \rho_q}}\right) = -\frac{1}{c_f}\Delta m$$

$$D = \frac{E_{lost,cycle}}{2\pi E_{stored,oscillator}}$$

m: mass
F/f_0: frequency/ fundamental frequency
μ_q: quartz shear modulus
ρ_q : quartz density
D: dissipation
E: energy

- **End-thiol-terminated PAA (M_n: 2,000-39,000 kDa)** is deposited onto gold QCM-D crystals to achieve a **self-assembled monolayer (SAM)** with various brush grafting densities, validated by **Variable Angle Spectroscopic Ellipsometry (VASE)**

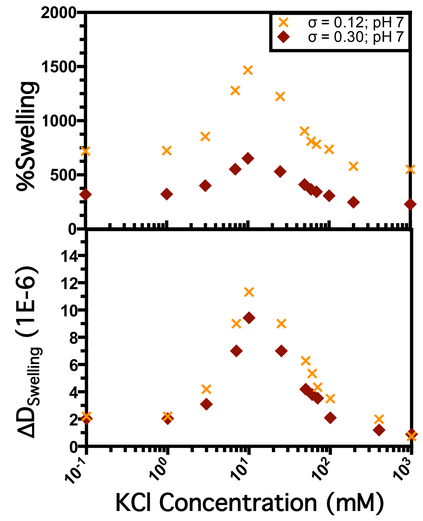
Results

Effect of Grafting Density

Densely grafted brushes→ less overall swelling in OB regime

Location of maximum swelling independent of grafting density

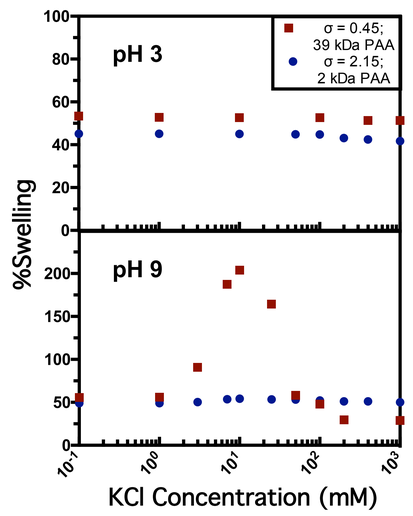
At high salt, brushes collapse to below their wet thickness at zero salt



Effect of pH & Chain Length

At pH 3 (<pKa), swelling not seen & brushes collapse slightly as salt increases

At pH 9 (>pKa) long brush swells and short brush is fully extended at high grafting densities



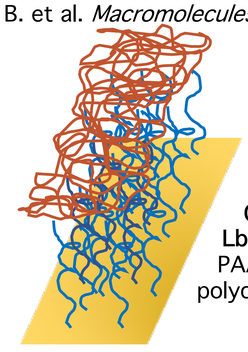
Hollingsworth, N. R. et al. *Soft Matter* **15**, 7838–7851 (2019)

Discussion & Future Directions

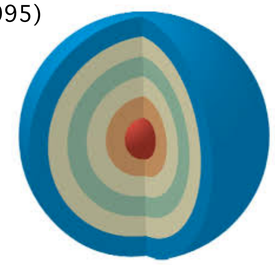
- Self-consistent field theory (SCFT) predicts the presence of two characteristic regimes:
  - **Osmotic brush (OB) regime:** osmotic pressure of associated counterions at low salt → **swelling**
  - **Salted brush (SB) regime:** charge screening from counterions at high salt → **collapse**
- Scaling exponents has been predicted to describe the effect on **height H** of varying **grafting density (σ)**, **chain length (N)**, & **salt concentration (Cs)**
- **Good agreement** is seen between experimentally obtained exponents (in the strongly charged limit) & those predicted by SCFT (see table) *except* in grafting density σ in the OB regime
- Next, QCM-D will be used to investigate an **LbL bilayer** of a PAA brush w/ **complementary polycation** to understand its equilibrium swelling given our current understanding of a single PAA brush layer

Theory	Scaling Prediction	Obtained Exponents
Strongly charged PE brushes[1]	OB→ $H\sim N\alpha^{1/2}$ SB→ $H\sim N\sigma^{\frac{1}{3}}C_s^{-\frac{1}{3}}$	OB→ N:1 ✓ σ: 0.18-0.31 ✗ C_S: 0.28-0.38 ✓
Weakly charged PE brushes[2]	OB→ $H\sim N\sigma^{-\frac{1}{3}}([H^+]+C_s)^{\frac{1}{3}}$ SB→ $H\sim N\sigma^{\frac{1}{3}}C_s^{-\frac{1}{3}}$	SB→ N: 1 ✓ σ: 0.33 ✓ C_S: -0.30 ✓

[1]Israels, R. et al. *Macromolecules* **27**, 3249–3261 (1994)
[2]Zhulina, E. B. et al. *Macromolecules* **28**, 1491–1499 (1995)



QCM-D LbL bilayer
PAA brush + polycation layer



LbL nanoparticle for targeted drug delivery

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