The Conformation of a Hydrophilic Di-block Copolymer on Silica

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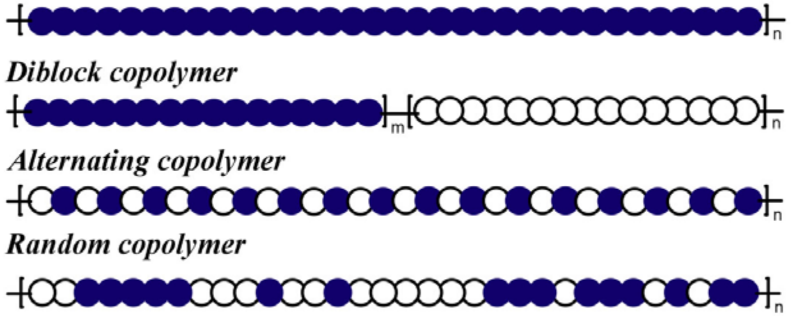
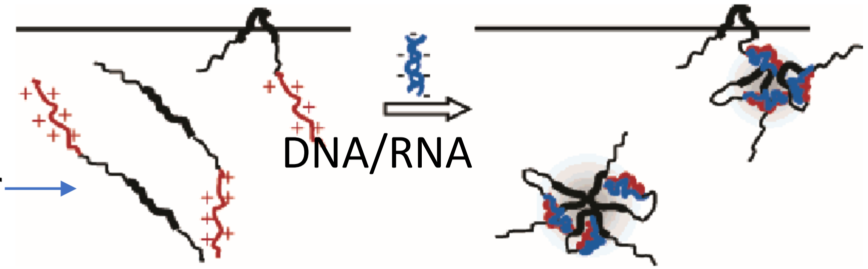
Mentors: John Riley and Michael Zhang

Background



Targeted drug delivery applications

Diblock Copolymer



(De)stabilize Colloidal Dispersions

https://www.wateronline.com/doc/understanding-separation-essentials-for-wastewater-treatment-0001

http://paintpad.com.au/wp-content/uploads/2015/11/paint.jpg

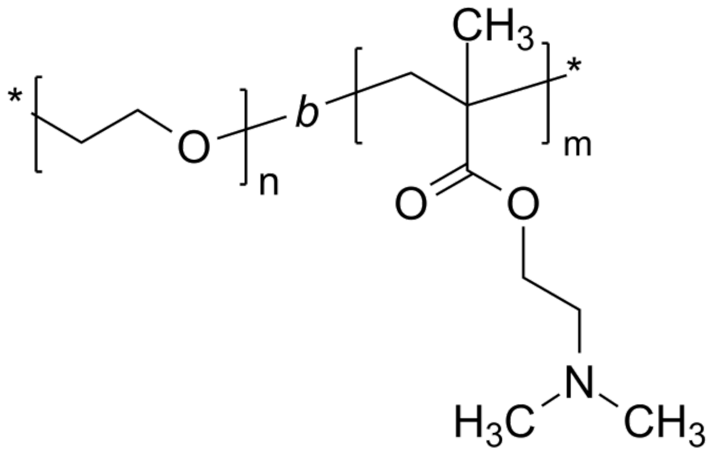
Waste Water Treatment

Paint

Interactions of diblock copolymers with surfaces and oppositely charged materials is of practical interest

Alvarez-Lorenzo, C.; Barreiro-Iglesias, R.; Concheiro, A.; Iourtchenko, L.; Alakhov, V.; Bromberg, L.; Temchenko, M.; Deshmukh, S.; Hatton, T. A. *Langmuir* **2005**, *21* (11), 5142–5148.

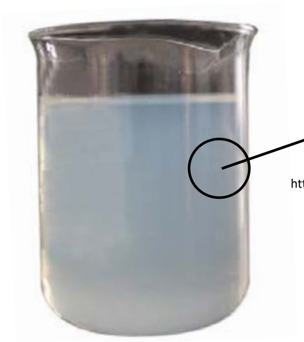
Di-Block Copolymer Adsorption on Silica

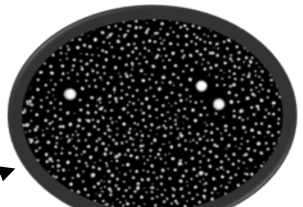


https://www.polymersource.ca/index.php?route=product/category&path=2_2190_17_131_953&subtract=1&categorystart=A-2.2.6.16&serachproduct=

Poly-ethylene oxide-poly(2-(dimethylamino) ethyl methacrylate)
(PEO(9500)-b-PDMA(9000))

Water Soluble





https://ec.europa.eu/jrc/en/science-update/first-certified-mixture-silica-nanoparticles (accessed Jul 23, 2018).

https://www.indiamart.com/proddetail/ludox-16213896088.html

Silica Nanoparticles

pH, salt concentration and concentration of silica and PEO-b-PDMA were varied

https://www.2spi.com/catalog/addimages/4176GSW-AB-2.jpg

Silicon Wafer

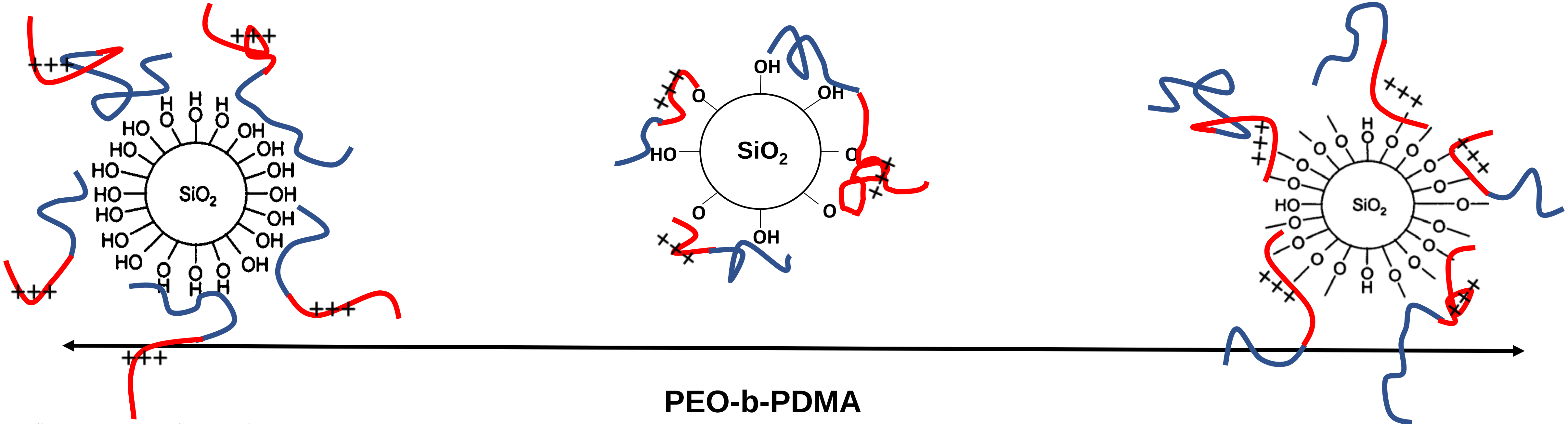
Surface charge varies with pH

Hypothesis

https://www.cmu.edu/maty/materials/Synthesis_of_well_defined_macromolecules/block-copolymers.html

PDMA
(interacts electrostatically with Si-O$^-$)

PEO
(interacts with Si-OH through hydrogen bonding)



https://patentimages.storage.googleapis.com/WO2008051616A2/imgf000019_0002.png

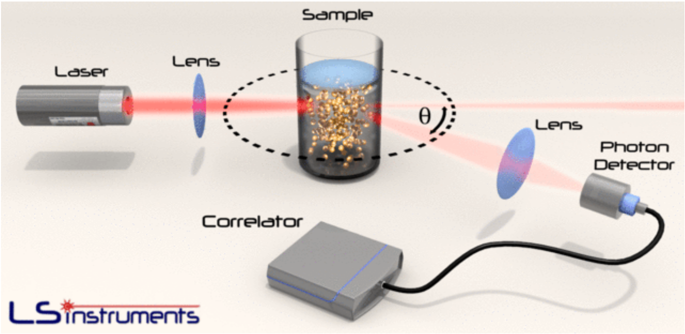
Acidic
(more Si-OH)

PEO-b-PDMA competition?

Basic
(more SiO$^-$)

Experimental Techniques

Dynamic Light Scattering (DLS)



https://lsinstruments.ch/index.php?--/frontend/handler/document.php=test&id=222

Size and Charge of Nanoparticles

Neutron Reflectometry

https://ncnr.nist.gov/instruments/ng7refl/

NG7 Reflectometer

Conformation of PEO-b-PDMA on Silica Wafer

Dynamic Light Scattering

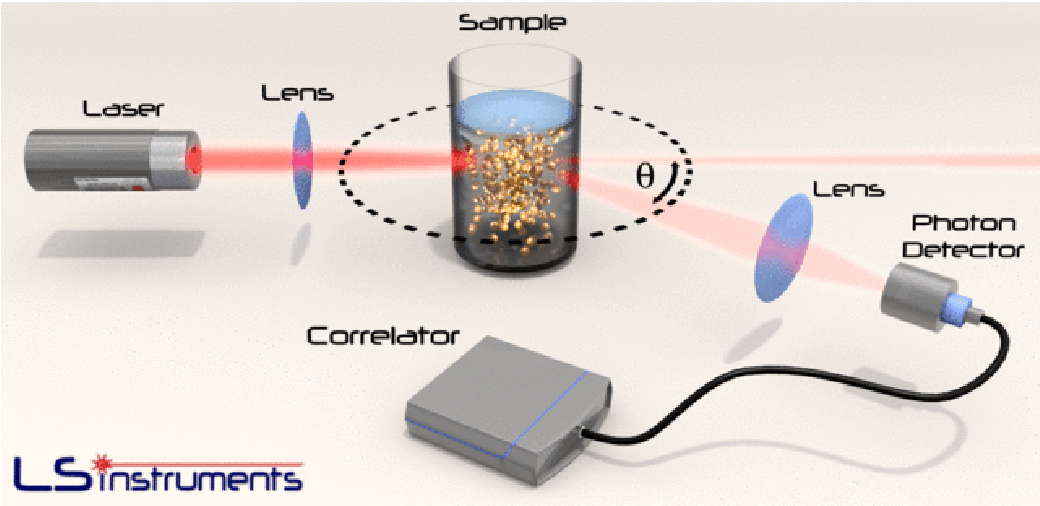
Technique used to obtain size and charge of a particle when suspended in solution

Particle size is related to diffusion coefficient through Stokes Einstein Equation

$$R_h = \frac{k_B T}{6\pi\eta_s D}$$

Charge of particle is related to electrophoretic mobility through modified Debye-Smoluchowski equation

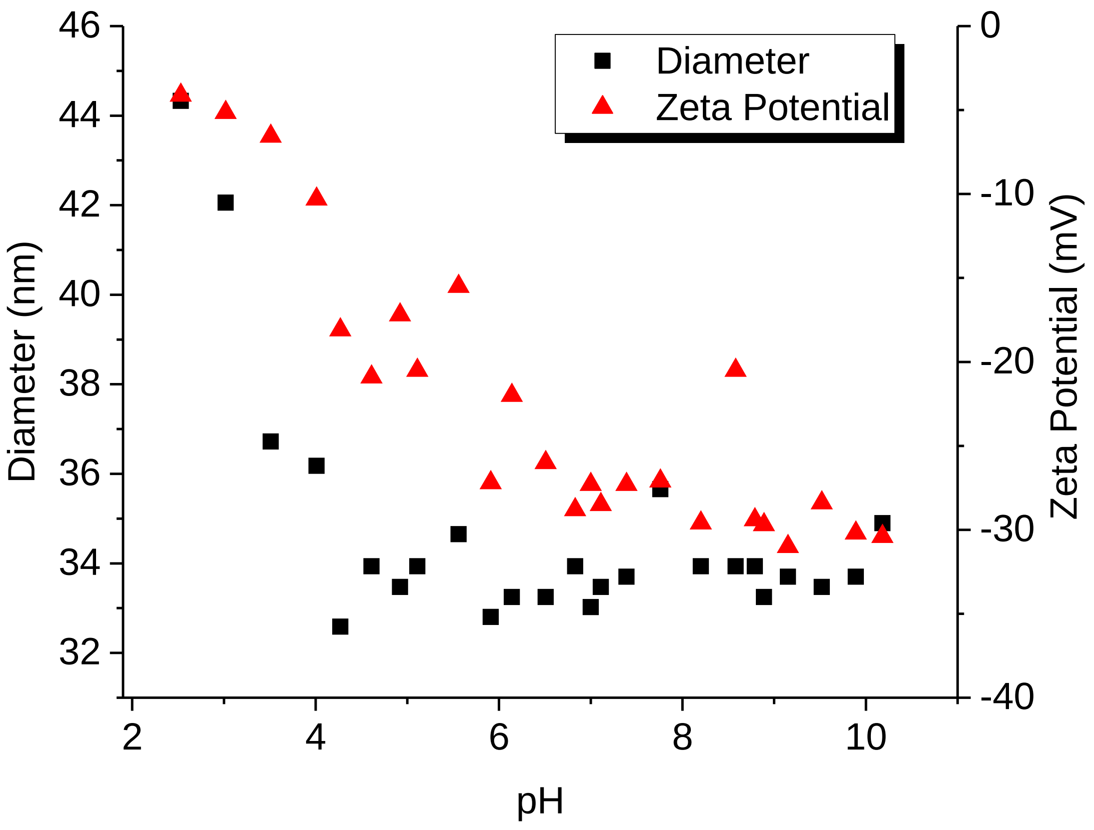
$$\mu_e = \frac{2\varepsilon_r\varepsilon_0\zeta}{3\eta_s} f(\kappa a)$$



Hassan, P. A.; Rana, S.; Verma, G. *Langmuir* **2014**, *31* (1), 3–12.

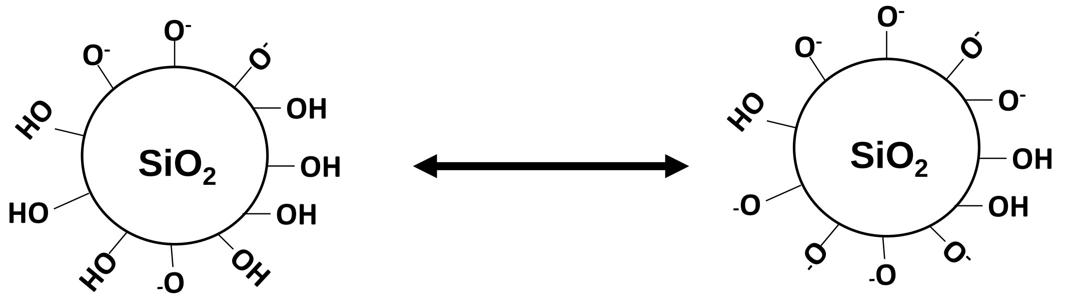
Szilagyi, I.; Trefalt, G.; Tiraferri, A.; Maroni, P.; Borkovec, M. *Soft Matter* **2014**, 10 (15), 2479.

pH Series of Bare Silica (.25 w/w%) at 10mM NaCl using DLS



Bare silica nanoparticles are stable between pH 4 and pH 10

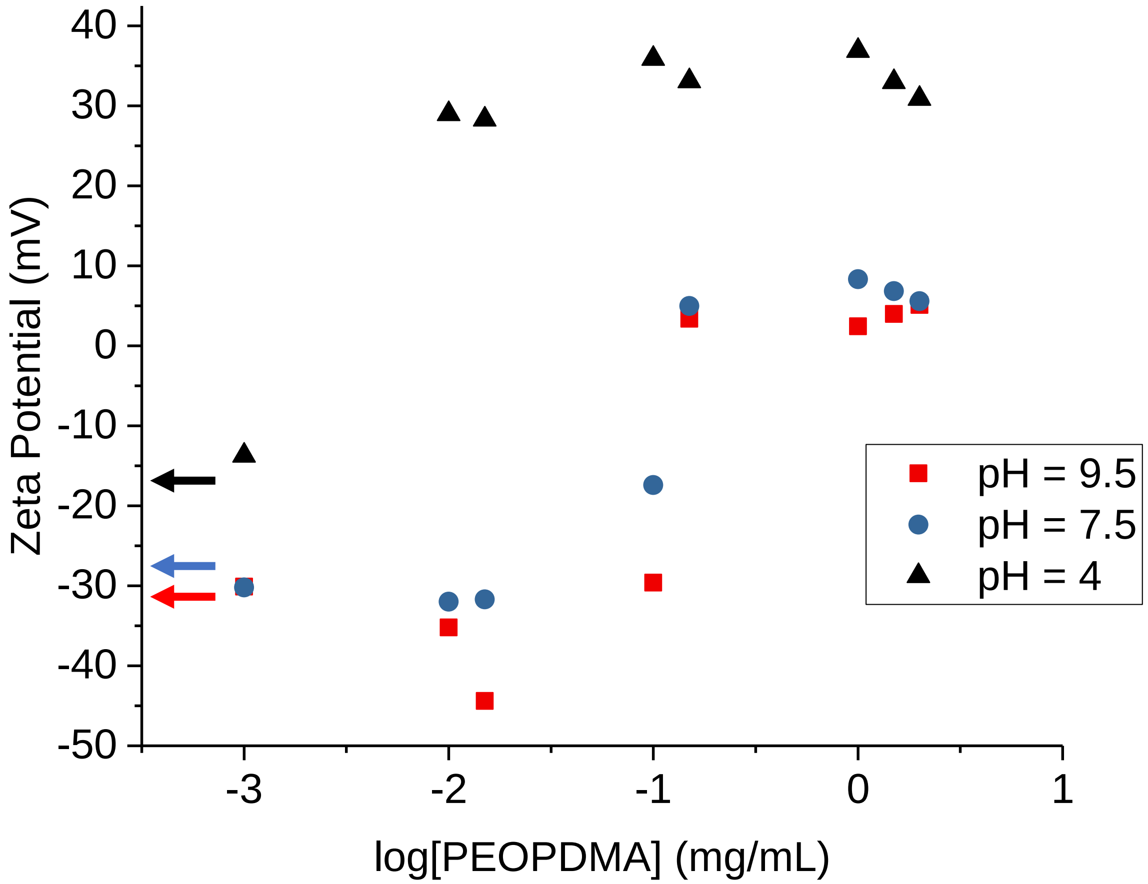
Provides baseline measurements for adsorbed polymer data

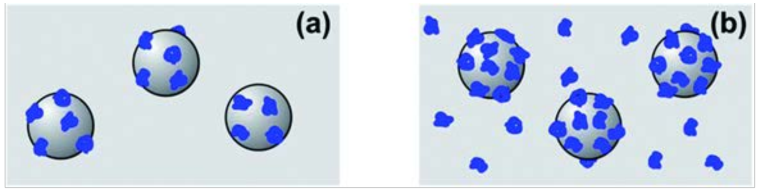


Acidic Conditions

Basic Conditions

Adsorption Isotherm for HPEO-b-HPDMA at 1mM NaCl





a) Unsaturated surface of particle
b) Saturated surface of particle

Saturation point of silica particles changes with pH.

Data indicates a strong charge reversal at lower pH and a weak charge reversal at high pH.

Szilagyi, I.; Trefalt, G.; Tiraferri, A.; Maroni, P.; Borkovec, M. *Soft Matter* **2014**, 10 (15), 2479.

Summary of DLS Results

DLS measurements are useful for detecting polymer adsorption onto oppositely charged silica nanoparticles.

The zeta potential of the silica particles changes based on the amount of PEO-b-PDMA adsorbed.

The data suggests that the diblock has a different conformation at pH 4 and pH 10 because of the extent of charge reversal.

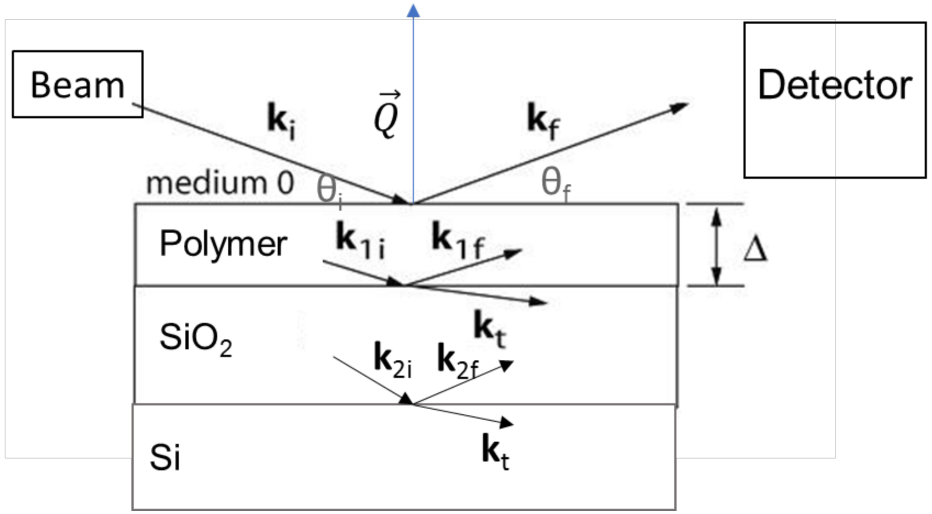
Neutron Reflectometry

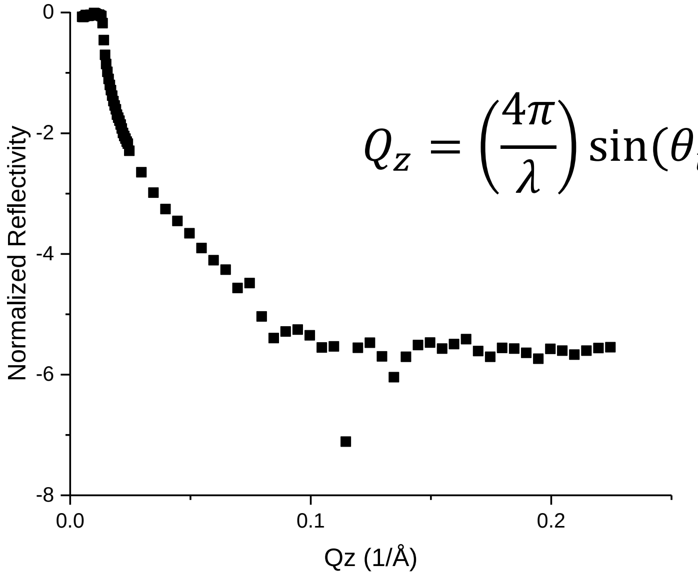
Technique that uses specular reflection to obtain reflectivity curves

Sensitive to differences in refractive indexes across surfaces and interfaces

Fit data to a theoretical model (slab, exponential model etc.), generating a scattering length density profile

Calculate layer thickness & roughness, which should change based on the block adsorbed onto the silica





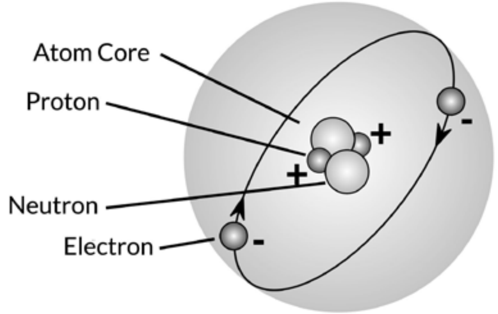
$$Q_z = \left(\frac{4\pi}{\lambda}\right)\sin(\theta_i)$$

Fitzsimmons, M. R.; Majkrzak, *C. F. Modern Techniques for Characterizing Magnetic Materials* 107–155.
Rodriguez-Loureiro, I.; Scoppola, E.; Bertinetti, L.; Barbetta, A.; Fragneto, G.; Schneck, E. *Soft Matter* **2017**, *13* (34), 5767–5777.

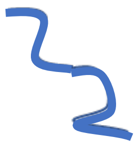
Neutron Reflectometry: Why neutrons?

Probes length scales of interest for adsorbed polymer layers (wavelength of neutron is 6 Angstroms)

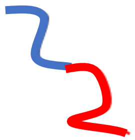
Highlight components of interest via selective deuteration/ contrast matching



http://animatedphysics.com/baryon_decay/xray_neutron_cross_section.png



HPEO-HPDMA

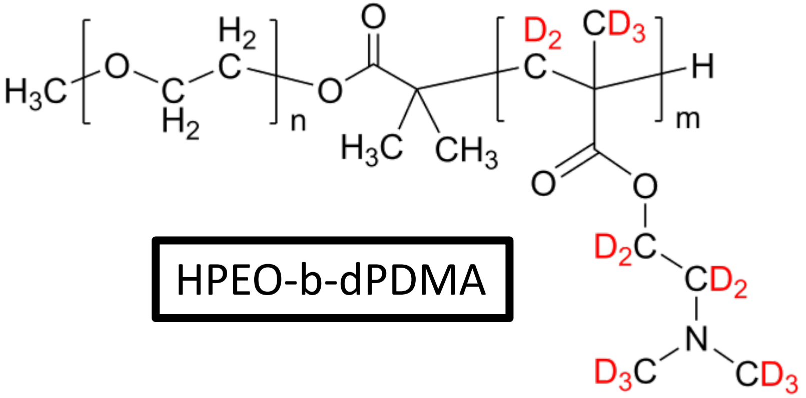


HPEO-dPDMA

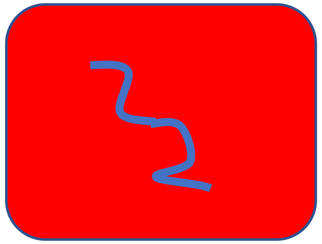
H_20

D_20

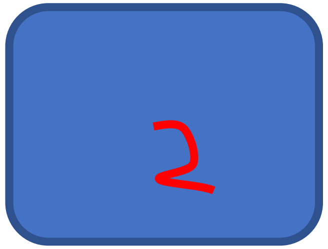
Solvents



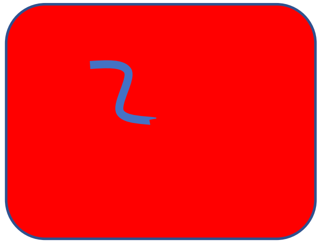
HPEO-b-dPDMA



HPEO-HPDMA in D_20



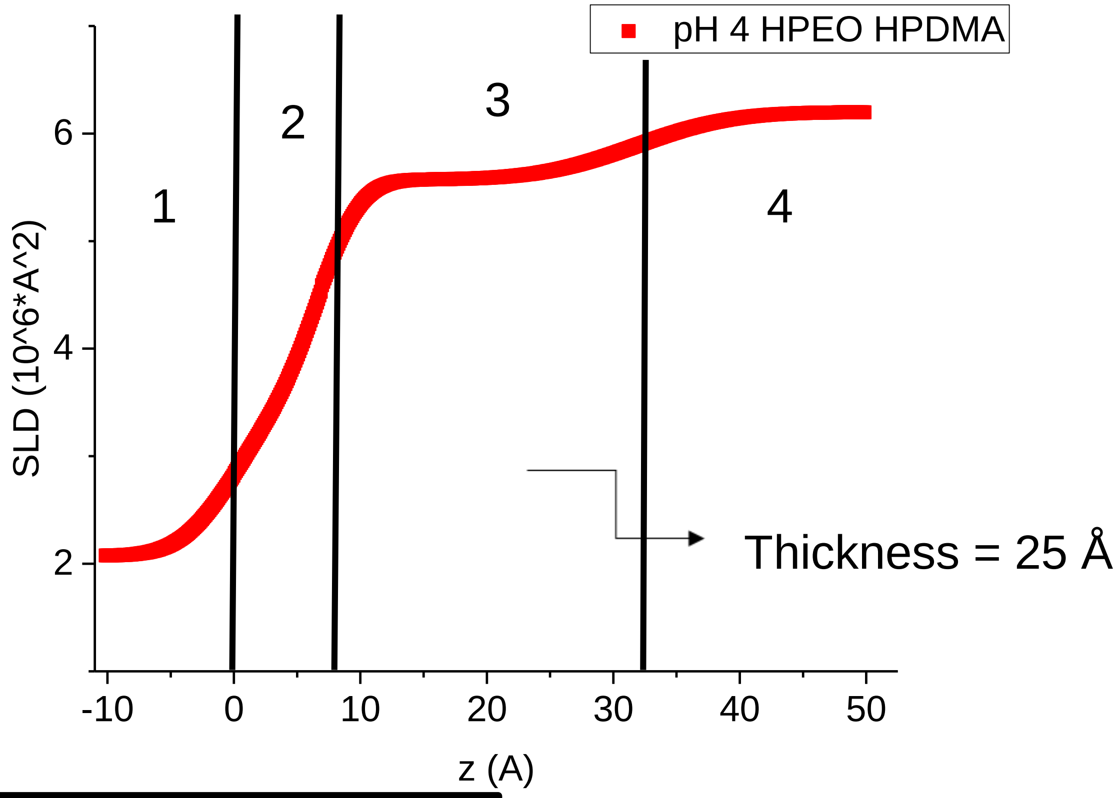
HPEO-dPDMA in H_20

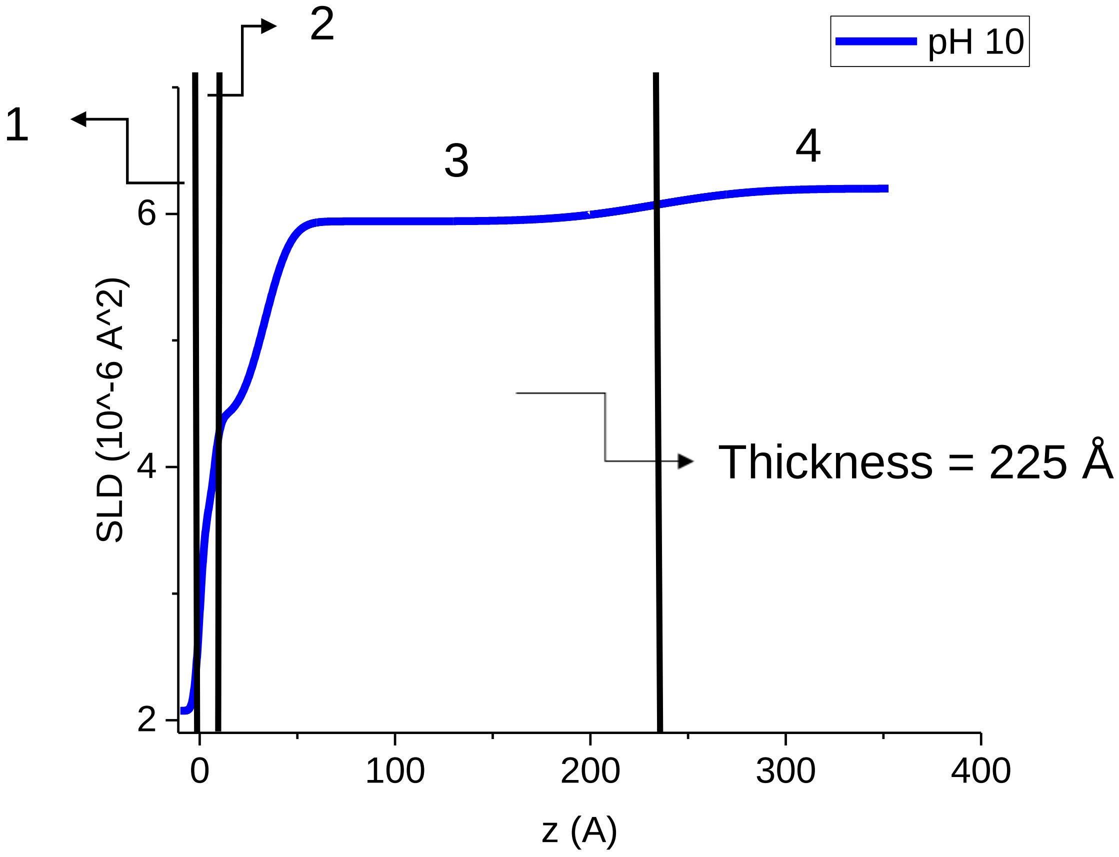


HPEO-dPDMA in D_20

https://www.polymersource.ca/index.php?route=product/category&path=2_2190_17_131_953&subtract=1&categorystart=A-2.2.6.16&serachproduct=

Scattering Length Density Profile of HPEO-b-HPDMA in D_2O

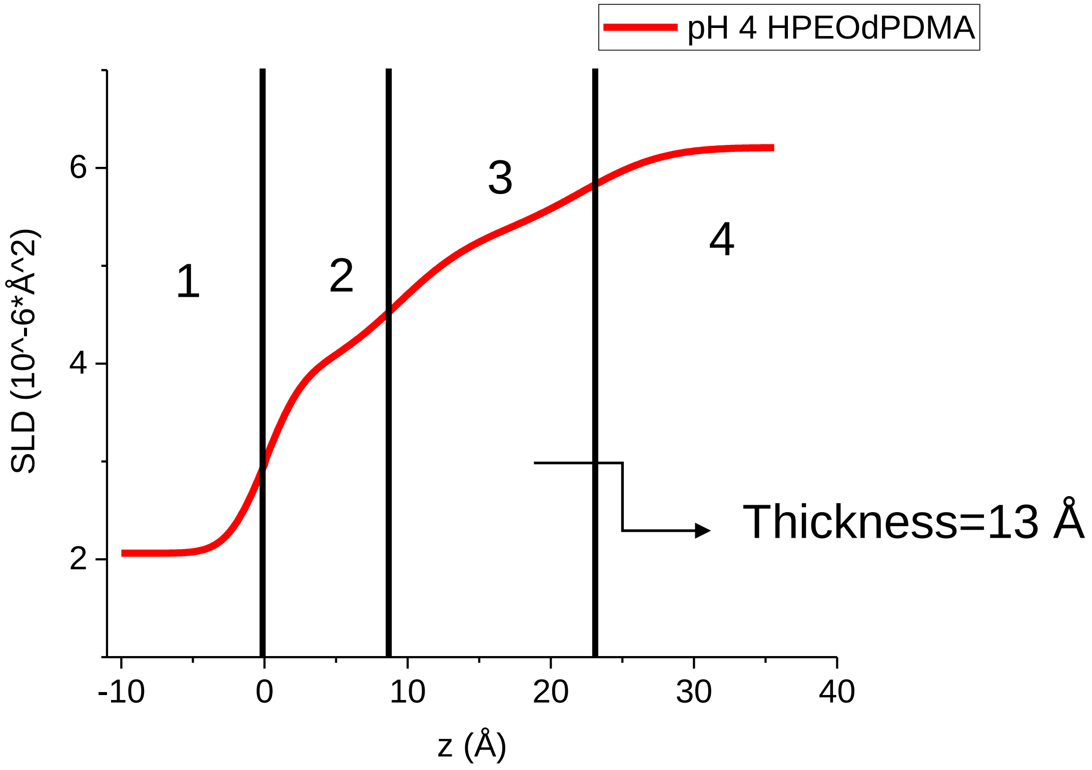


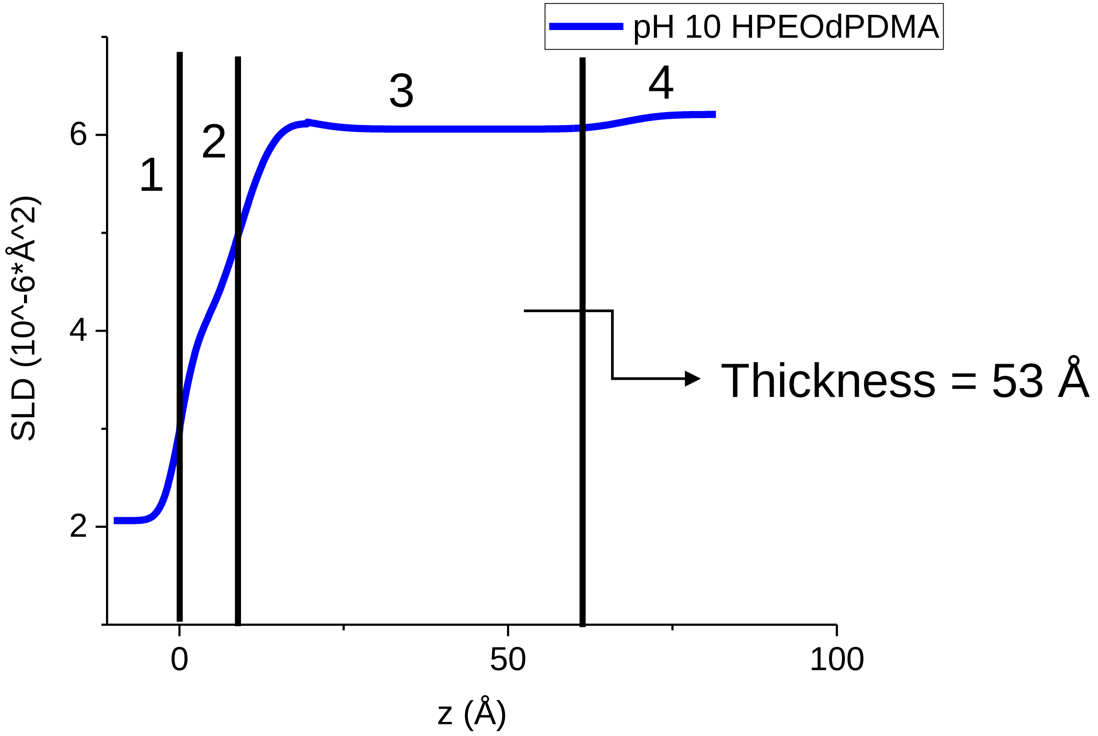


1 = Si Layer
2 = SiO_2 Layer
3 = HPEO-HPDMA Layer
4 = D_2O Layer

***Entire* HPEO-HPDMA layer** is significantly thicker at pH 10 compared to pH 4.

Scattering Length Density Profile of HPEO-b-dPDMA in D_2O





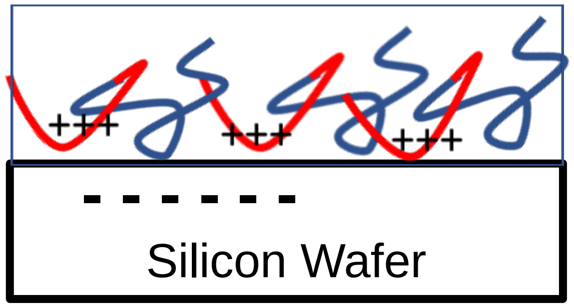
1 = Si Layer
2 = SiO_2 Layer
3 = HPEO-dPDMA Layer
4 = D_2O Layer

The positioning of the HPEO block at pH 10 is significantly extended away from the interface compared to pH 4.
HPEO is less attracted to surface of the silicon wafer at pH 10.

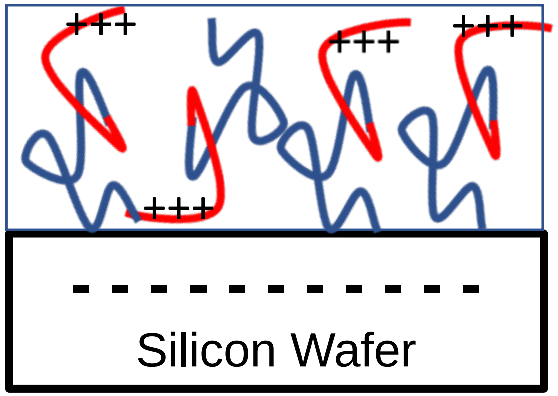
Summary of Neutron Reflectometry Results

The conformation of the di-block copolymer is different at pH 4 and pH 10, which is supported by the varying thickness of the polymer layer adsorbed onto the silica wafer.

pH 4 may not be acidic enough for the PEO block to be the main adsorbed block, the polymer may be laying flat.



pH 4



pH 10

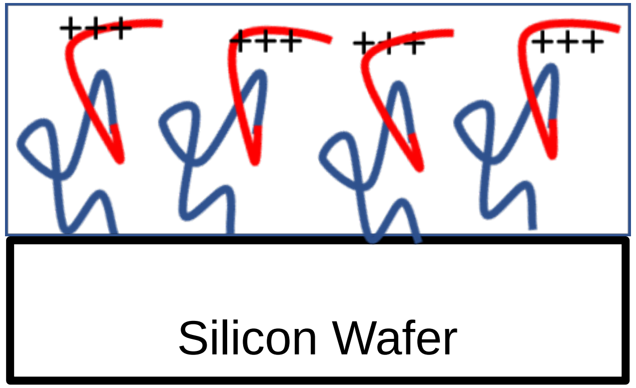
Future Work

Further model and improve fits on neutron reflectometry data to get a more accurate thickness, especially at pH 10.

Complement reflectometry data with Quartz Crystal Microbalance with Dissipation (QCM-D) measurements to obtain mass and swelling of the adsorbed layer.

Run experiments at pH 2 to see if there is another conformational change.

https://openqcm.com/wp-content/uploads/2015/02/Quartz-crystal-Microbalance-openQCM-Sensor-1208x440.jpg



pH 2??

Acknowledgements

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Center for High Resolution Neutron Scattering

NCNR SURFers ☺

Reflectivity Curves