2016 U.S. Frontiers of Engineering Symposium
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Scalable Manufacturing of Layer-by-Layer Membranes for Water Purification

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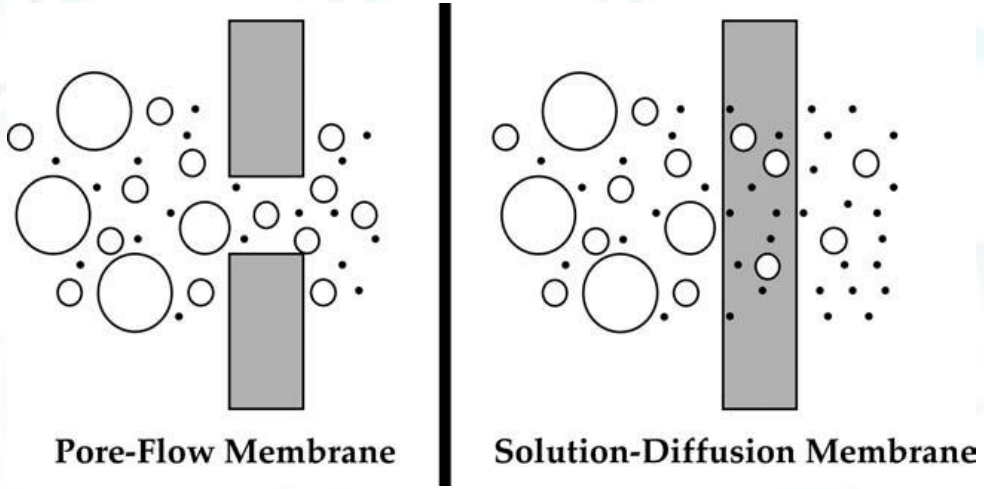
National Institute of Standards and Technology

NIST
National Institute of Standards and Technology
U.S. Department of Commerce

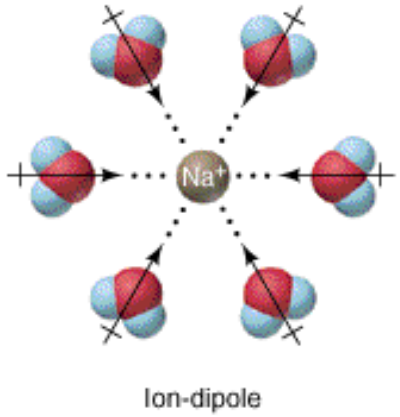
MATERIAL MEASUREMENT LABORATORY

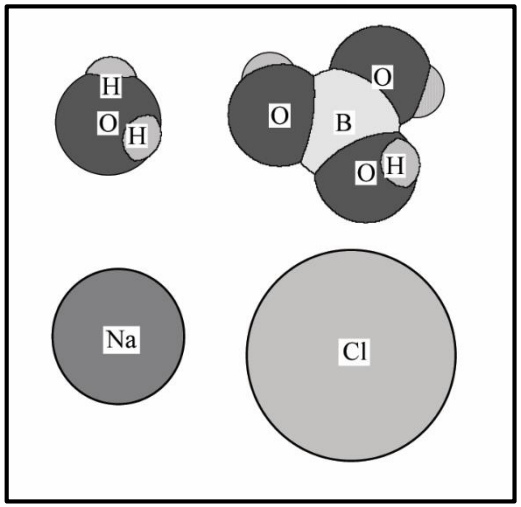
MEMBRANES FOR DESALINATION



molecular size

H_2O	2.8 Å
Na^+	2.0 Å
hydrated Na^+	7.9 Å

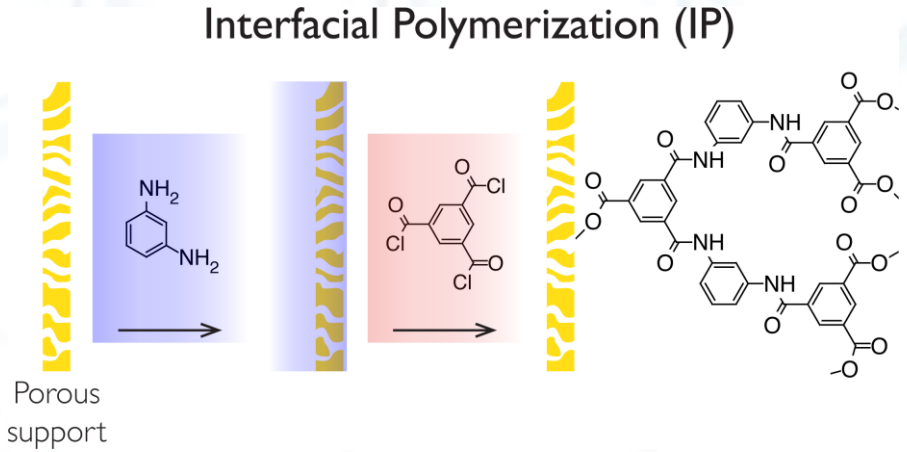




OVERVIEW

- Thin film composite (TFC) membranes
- Current (TFC) innovations
- Measurement innovations
- Opportunities

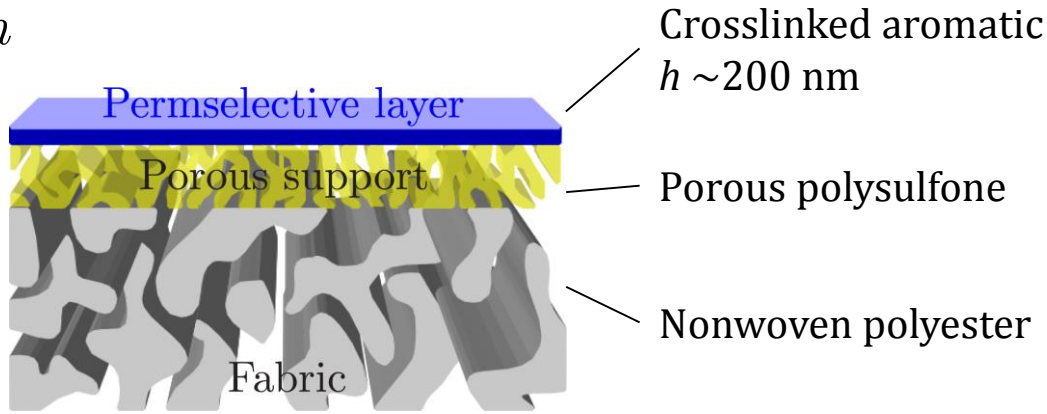
THIN FILM COMPOSITE MEMBRANES (TFC)



Membrane active layer has to be:

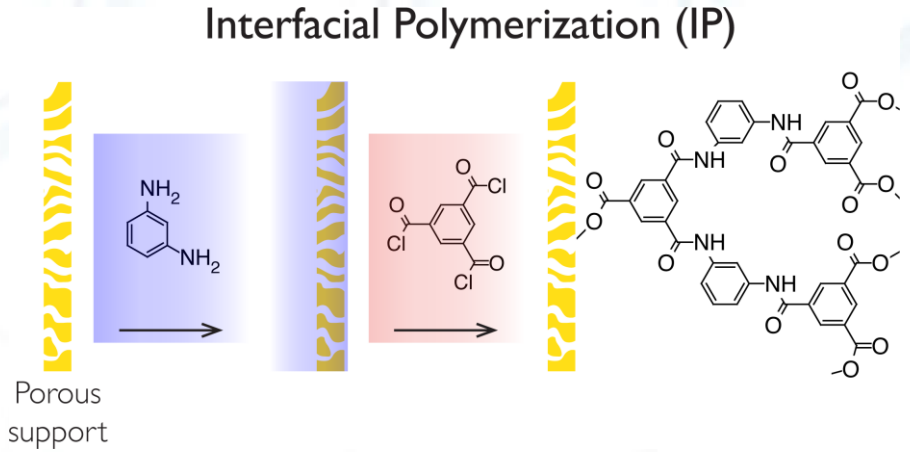
- incredibly thin (10s – 100s nm)
- defect free
- mechanically robust
- chlorine tolerant
- fouling resistant

$$J_{water} \propto \frac{1}{h}$$



Thin film composite (TFC)

THIN FILM COMPOSITE MEMBRANES (TFC)



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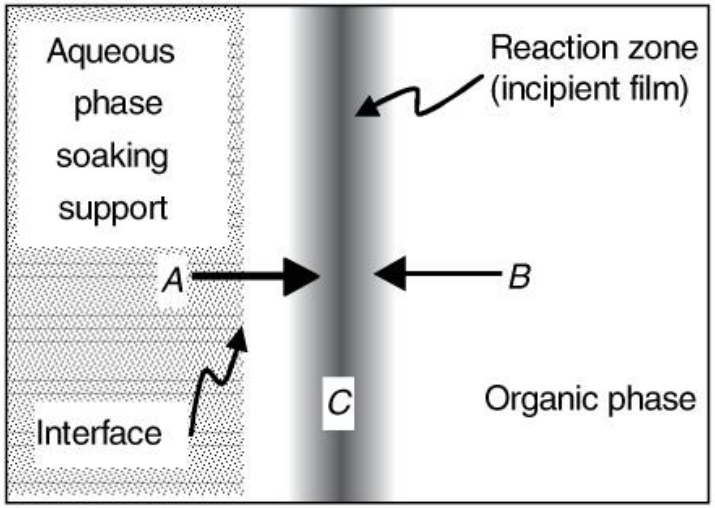

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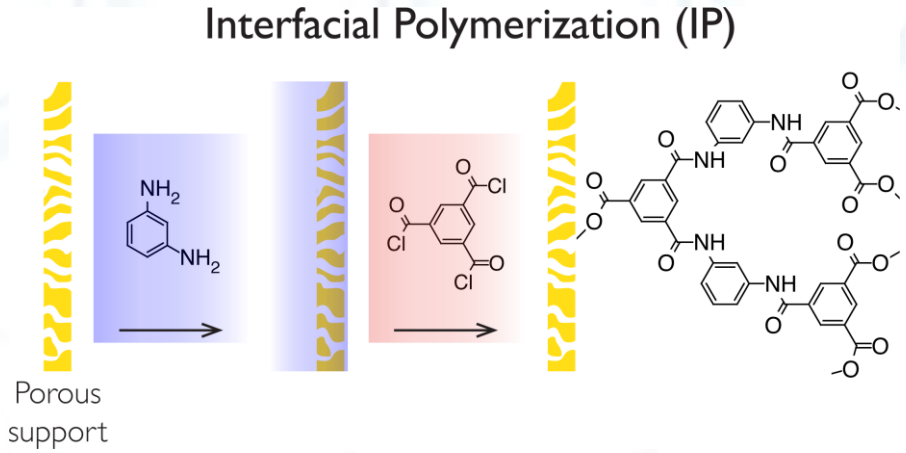
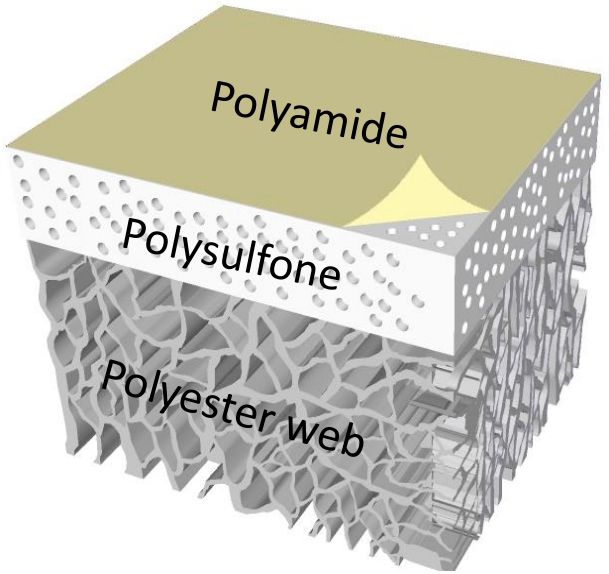
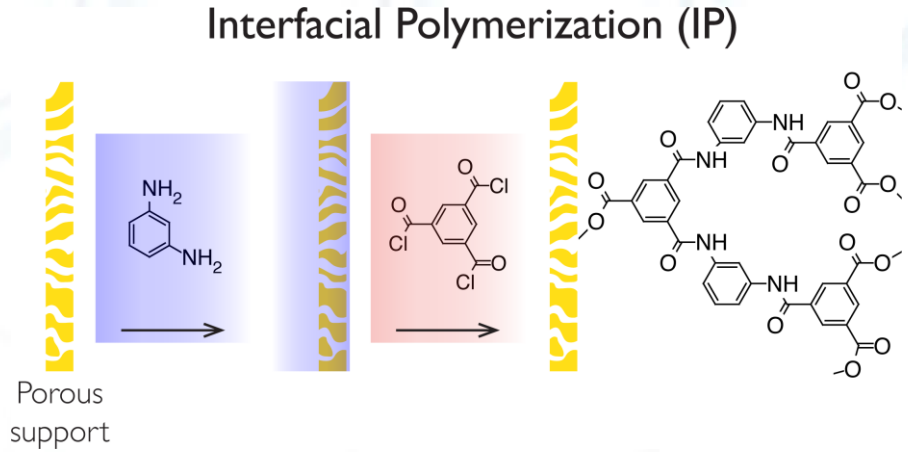


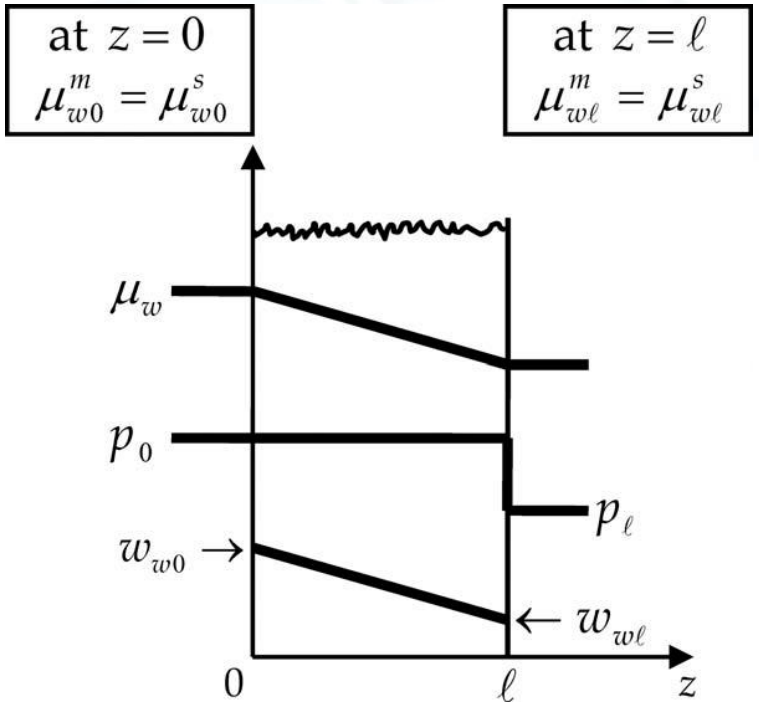
Membrane technologist sees:



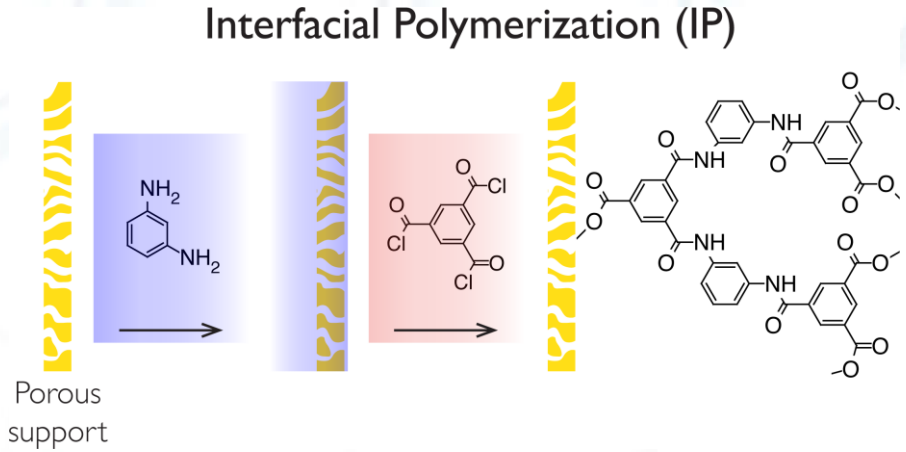
THIN FILM COMPOSITE MEMBRANES (TFC)



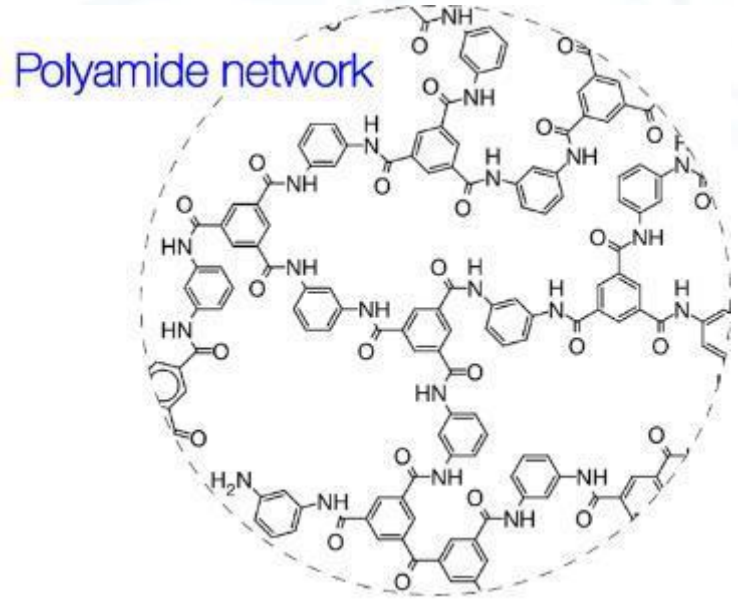
Chemical engineer sees:



THIN FILM COMPOSITE MEMBRANES (TFC)



Polymer scientist sees:



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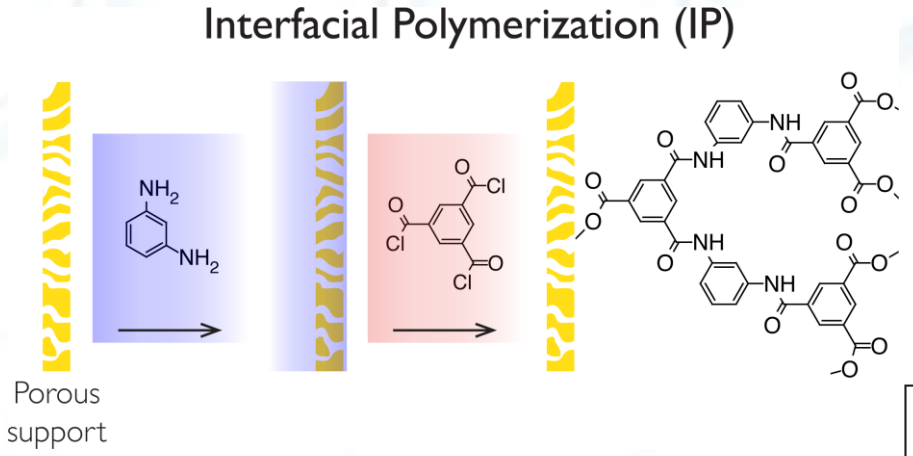
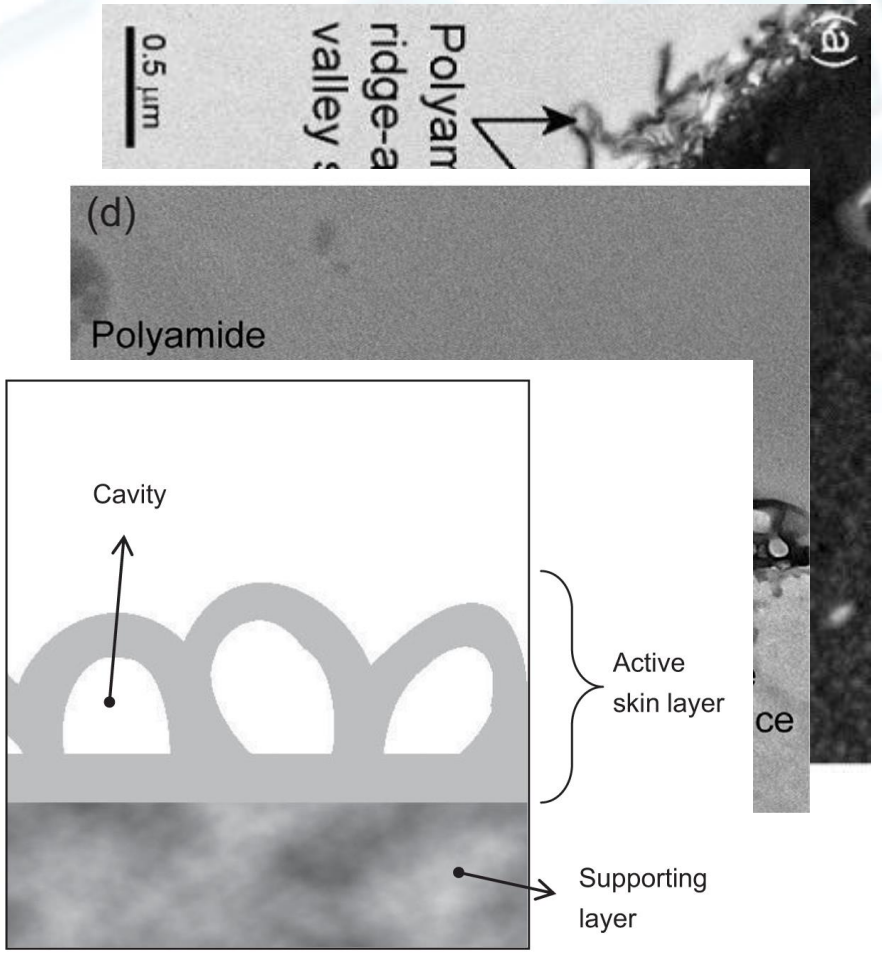


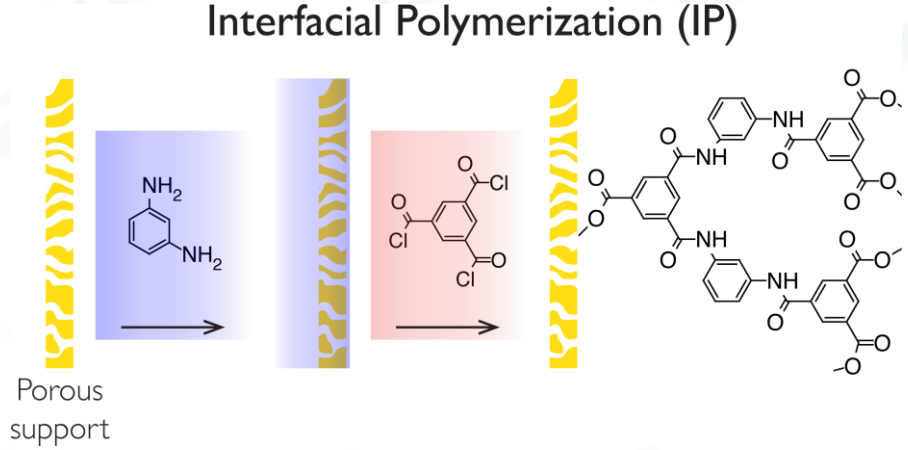


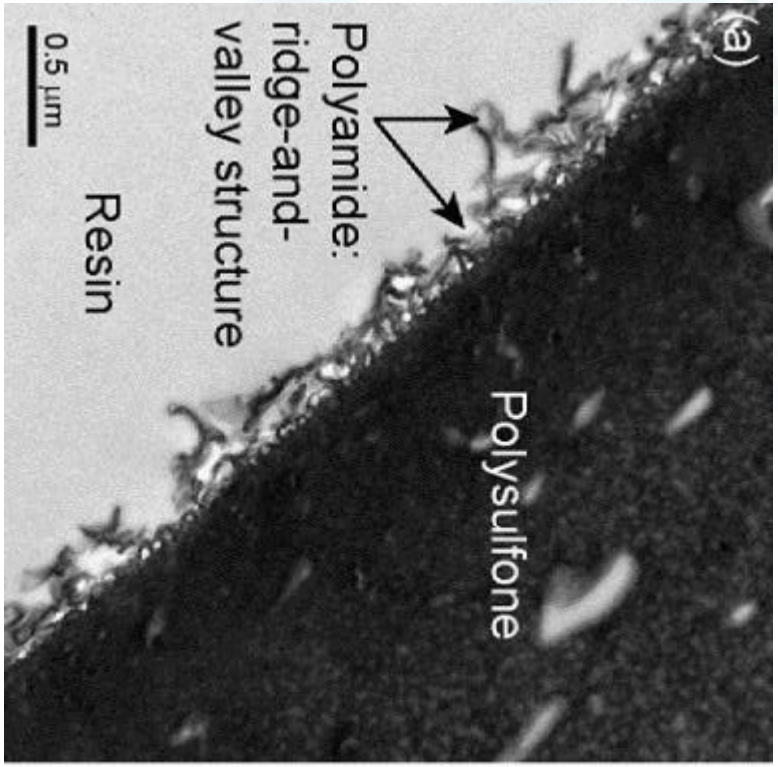
"The lack of correlation between film thickness and permeability suggests the entire film thickness may not contribute to separation"

- *J. Membrane Sci.* **311**, 34-45 (2008)

Fig. 3. Schematic cross-sectional image of the active skin layer of an RO membrane.

THIN FILM COMPOSITE MEMBRANES (TFC)





Chemistry/process has not changed much in 40 years….

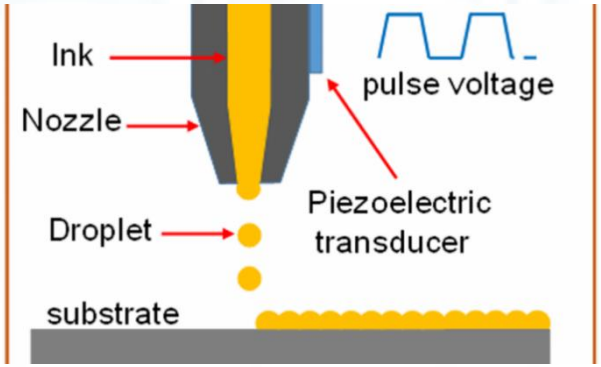
Analytical tools and polymer science have outpaced this technology.

OVERVIEW

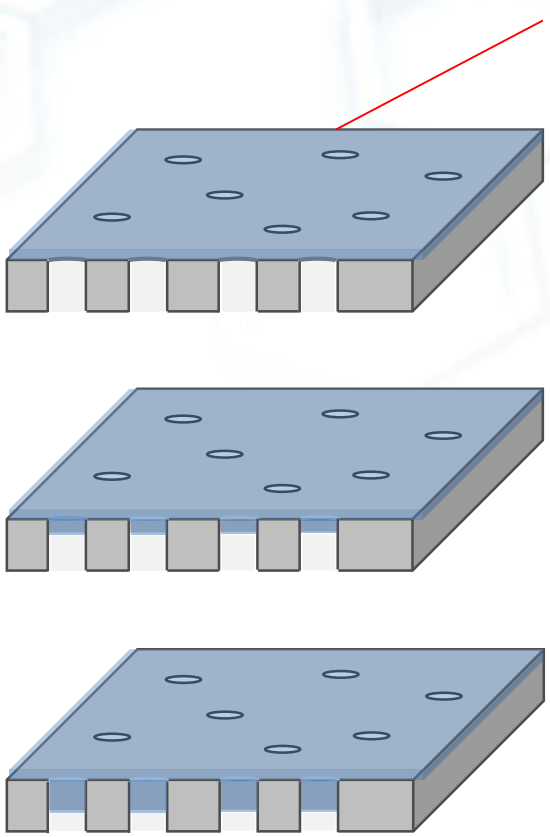
- Thin film composite (TFC) membranes
- Current (TFC) innovations
- Measurement innovations
- Opportunities

MEMBRANE INNOVATION – TWEAKING THE PROCESS

Inkjet printing was used to control dosing (concentration) of amine available for interfacial polymerization



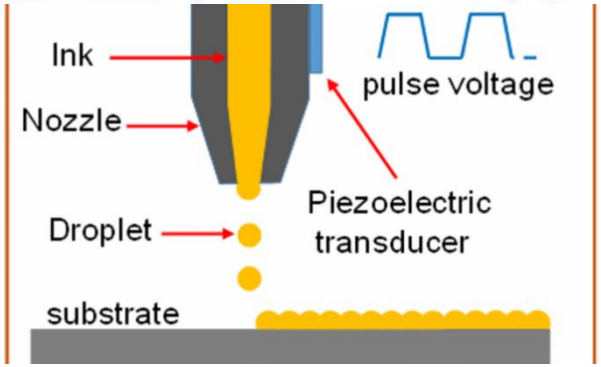
- Multiple passes of the inkjet printer leads to increased dose of amine solution available for polymerization



S. Badalov and C.J. Arnusch; *J Memb Sci* **2016**, 515, 79.

MEMBRANE INNOVATION – ADJUSTING DEPOSITION

Inkjet printing was used to control dosing (concentration) of amine available for interfacial polymerization



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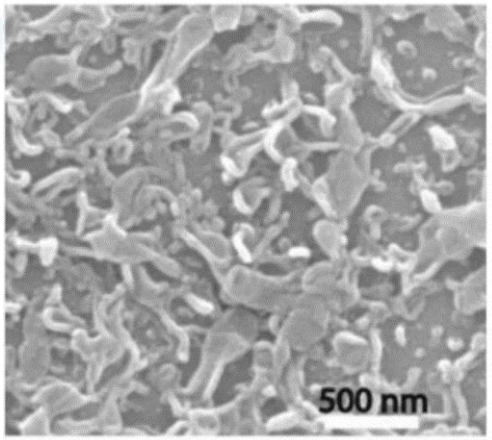
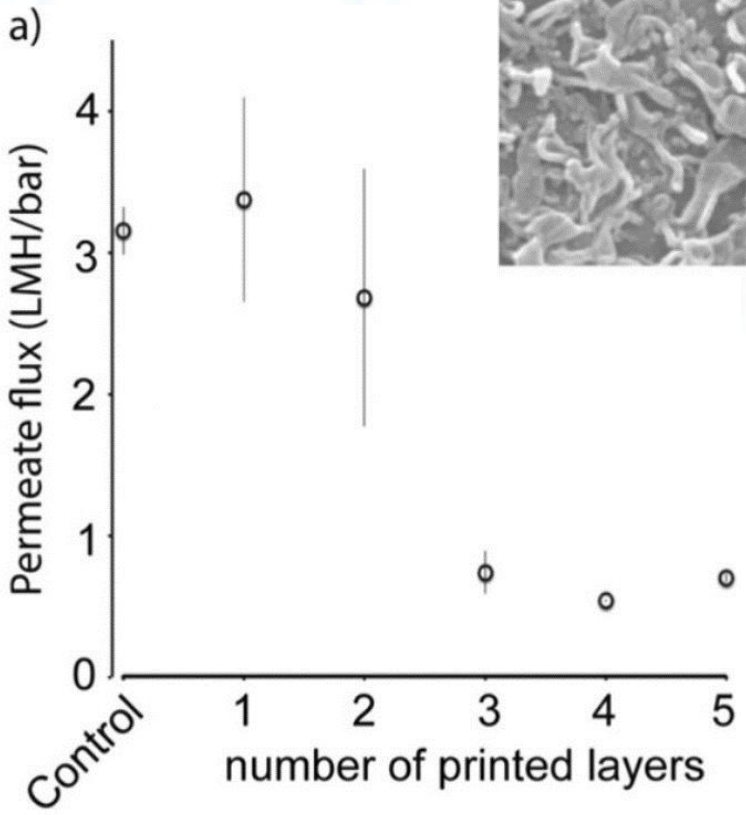
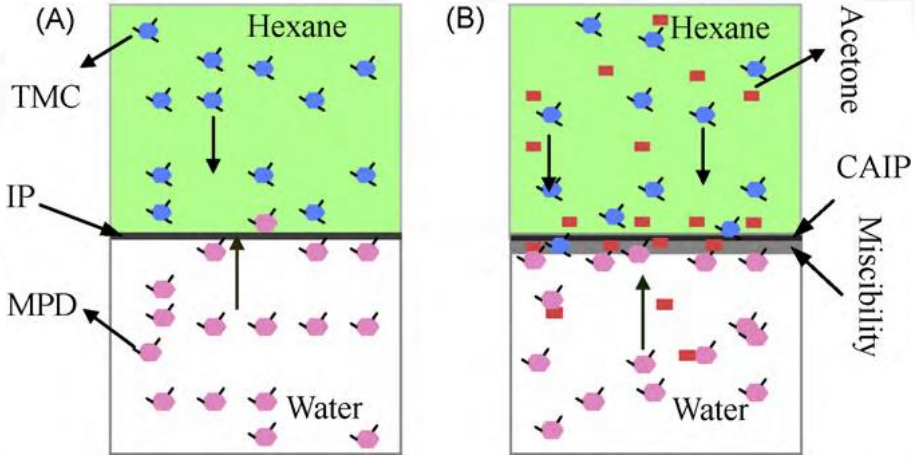




S. Badalov and C.J. Arnusch; *J Memb Sci* **2016**, 515, 79.

MEMBRANE INNOVATION – ALTERING REACTION ZONE

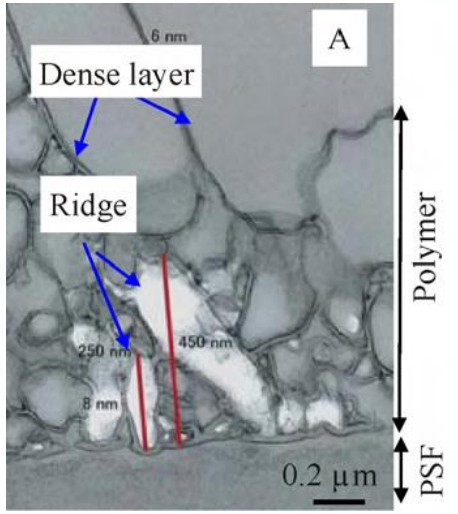
Co-solvent assisted interfacial polymerization (CAIP)



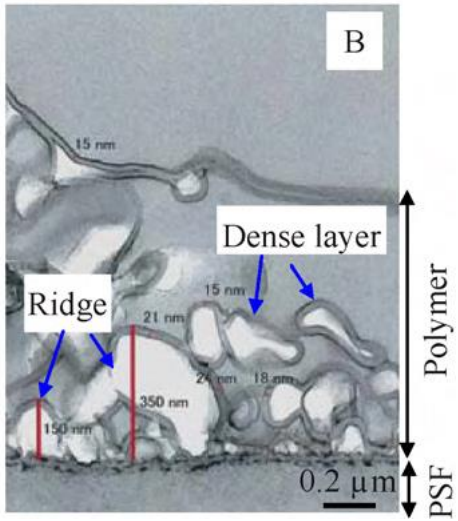
- Addition of a co-solvent in the organic phase
- Controls the miscibility and/or solubility of the amine at the interface of the two immiscible fluids

C. Kong et al.; *J Memb Sci* **2010**, 362, 76.

CAIP

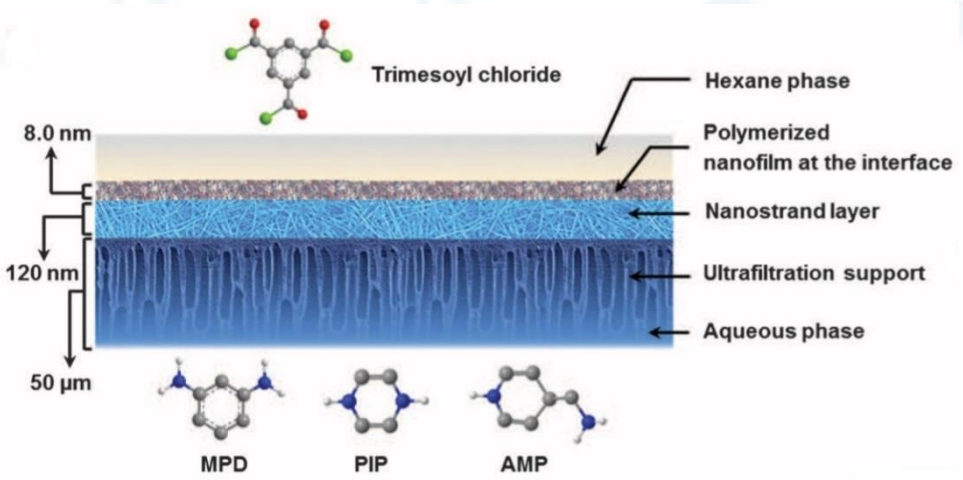


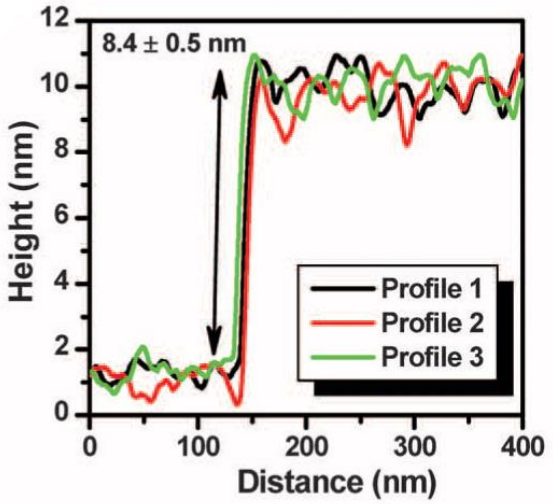
IP



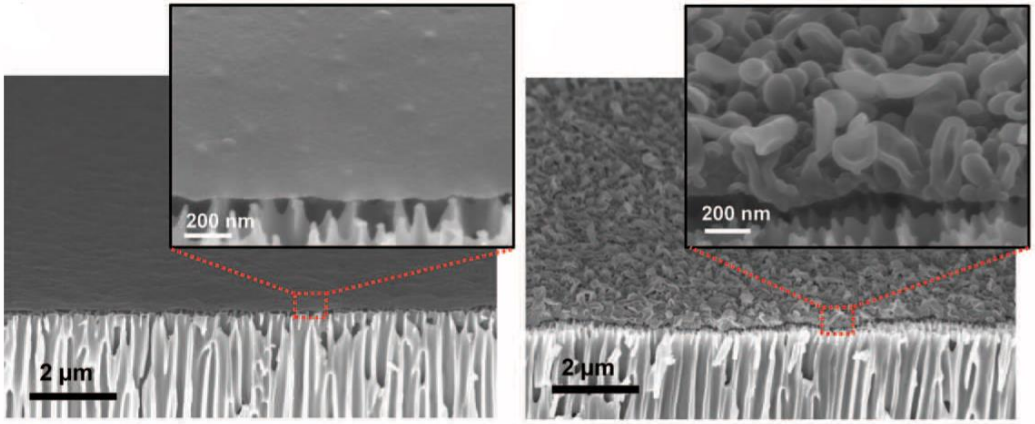
MEMBRANE INNOVATION – ALTERING THE SUPPORT

Sacrificial nanofiber layer [$Cd(OH)_2$)]



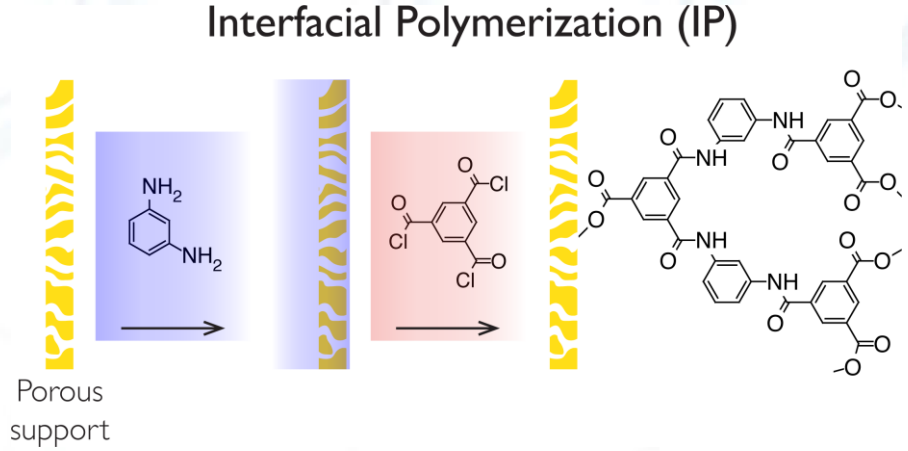


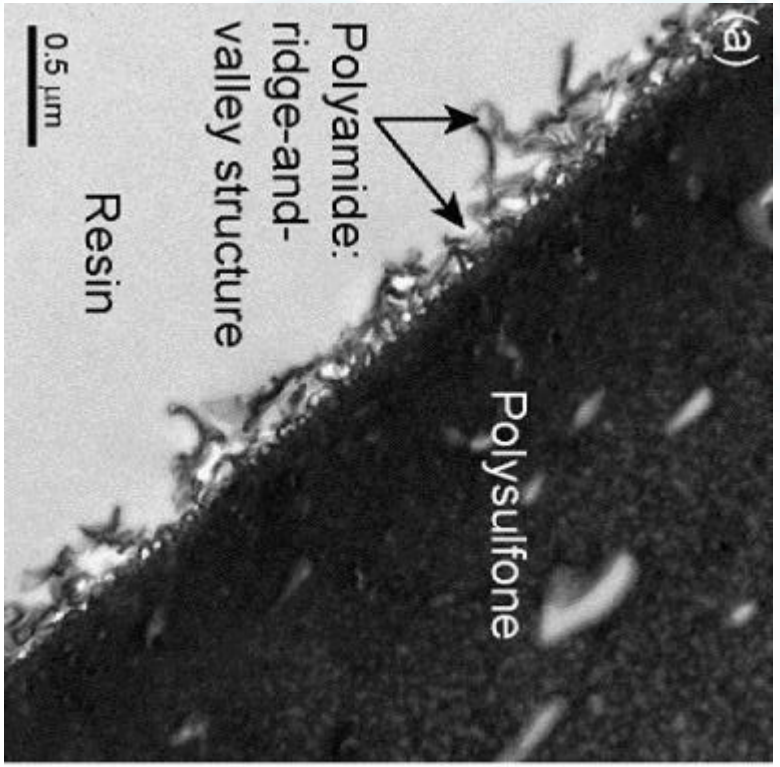
- Cadmium hydroxide nanostrands act to gate amine arrival at the interface
- Nanostrands can then be removed via acid treatment



S. Karan et al.; *Science* **2015**, 348, 1347.

THIN FILM COMPOSITE MEMBRANES (TFC)





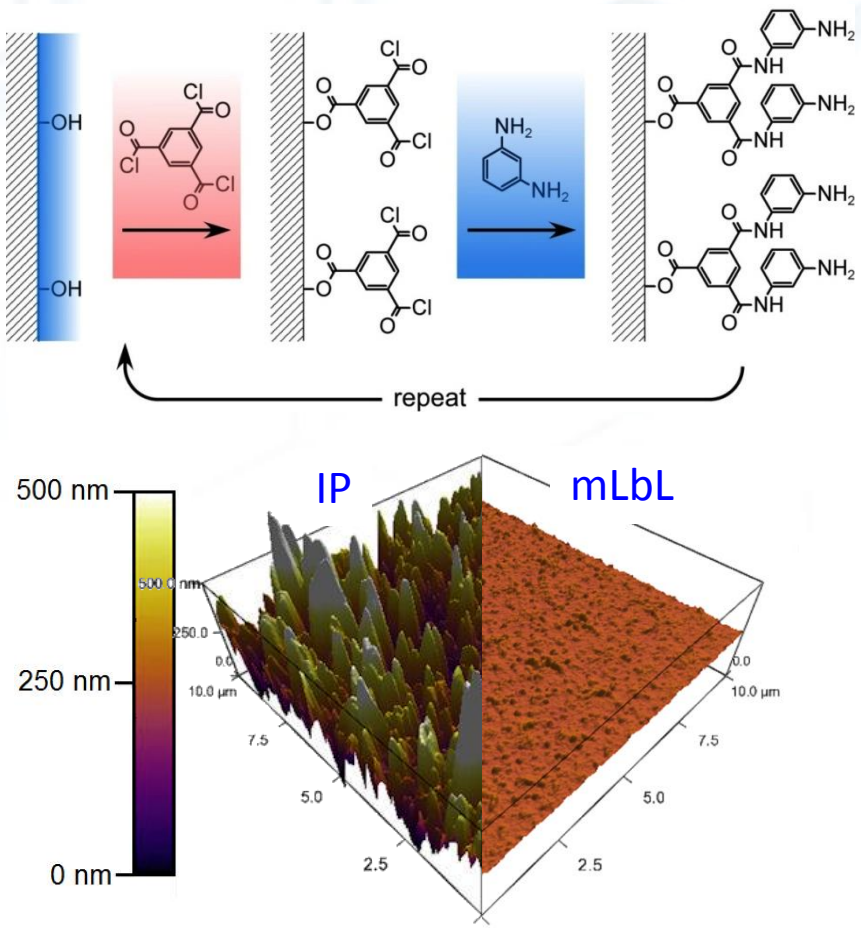
How do we measure something like this?

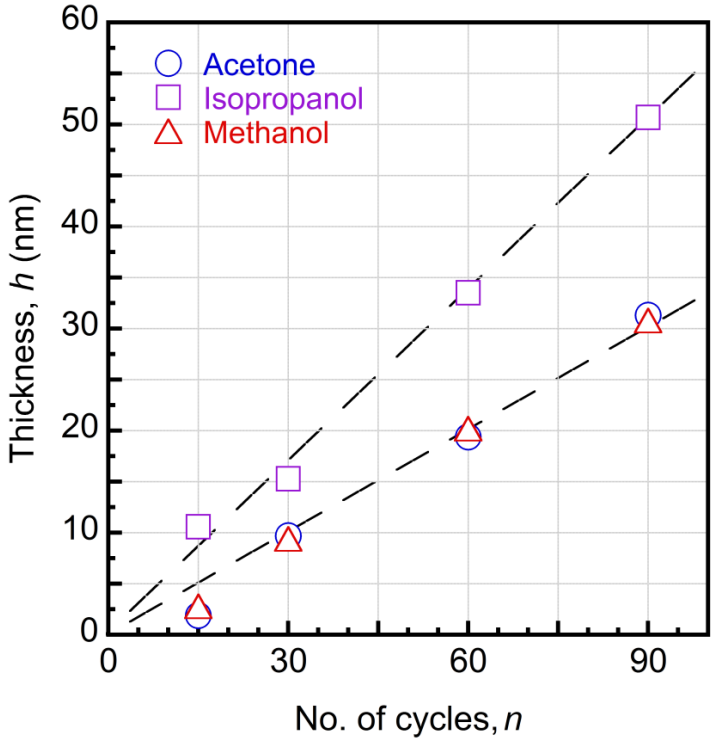
Can we provide a platform for fundamental measurements of structure/property/transport?

MEMBRANE INNOVATION – DISRUPTIVE TECHNOLOGY

FUNCTIONAL POLYMERS

molecular Layer-by-Layer (mLbL)





P. M. Johnson, et al.; *JPSB* **2011**, 50, 168.

MEMBRANE INNOVATION – DISRUPTIVE TECHNOLOGY

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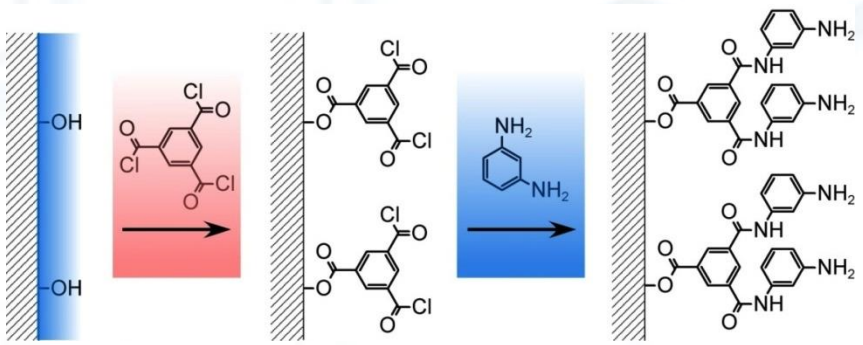
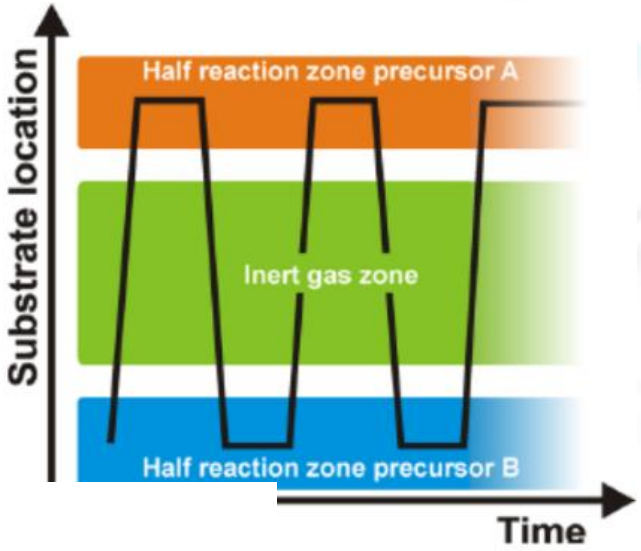
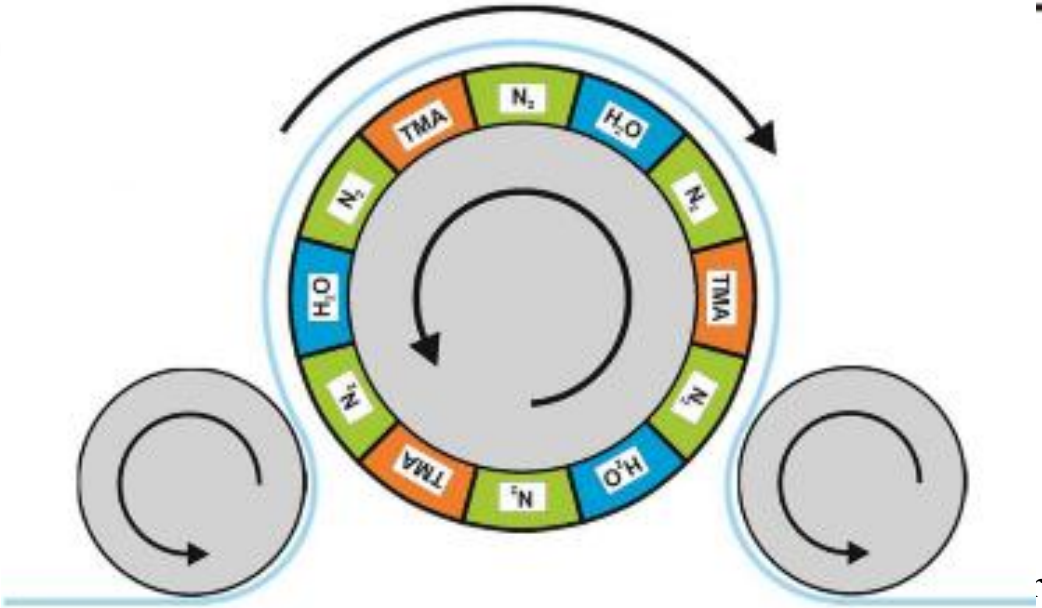


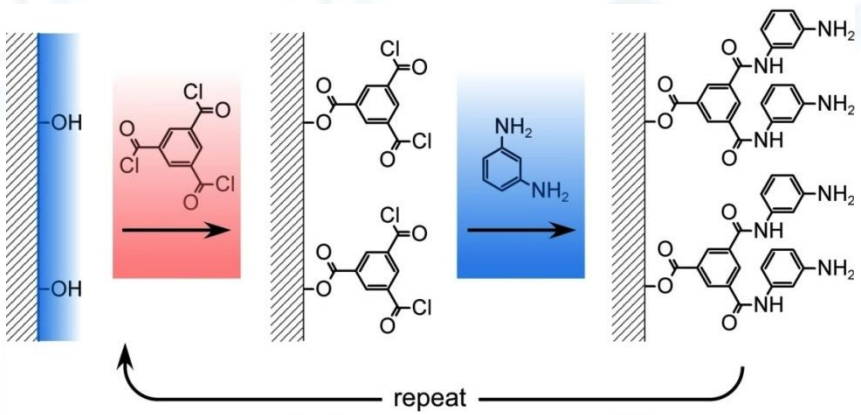




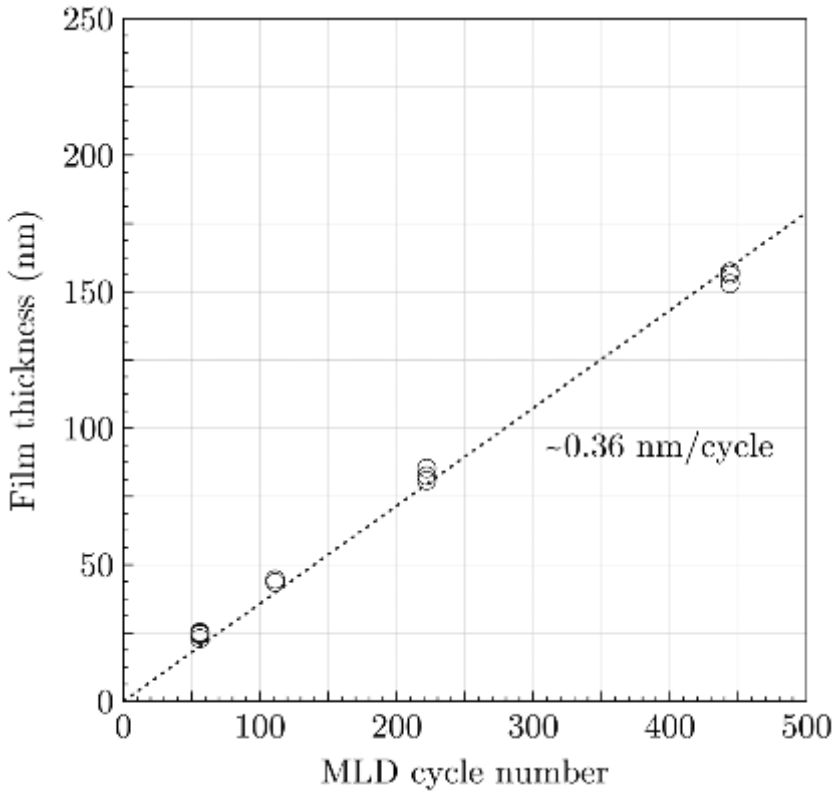
ge and D. Higgs, UC Boulder.

MEMBRANE INNOVATION – DEMONSTRATION

molecular Layer-by-Layer (mLbL)



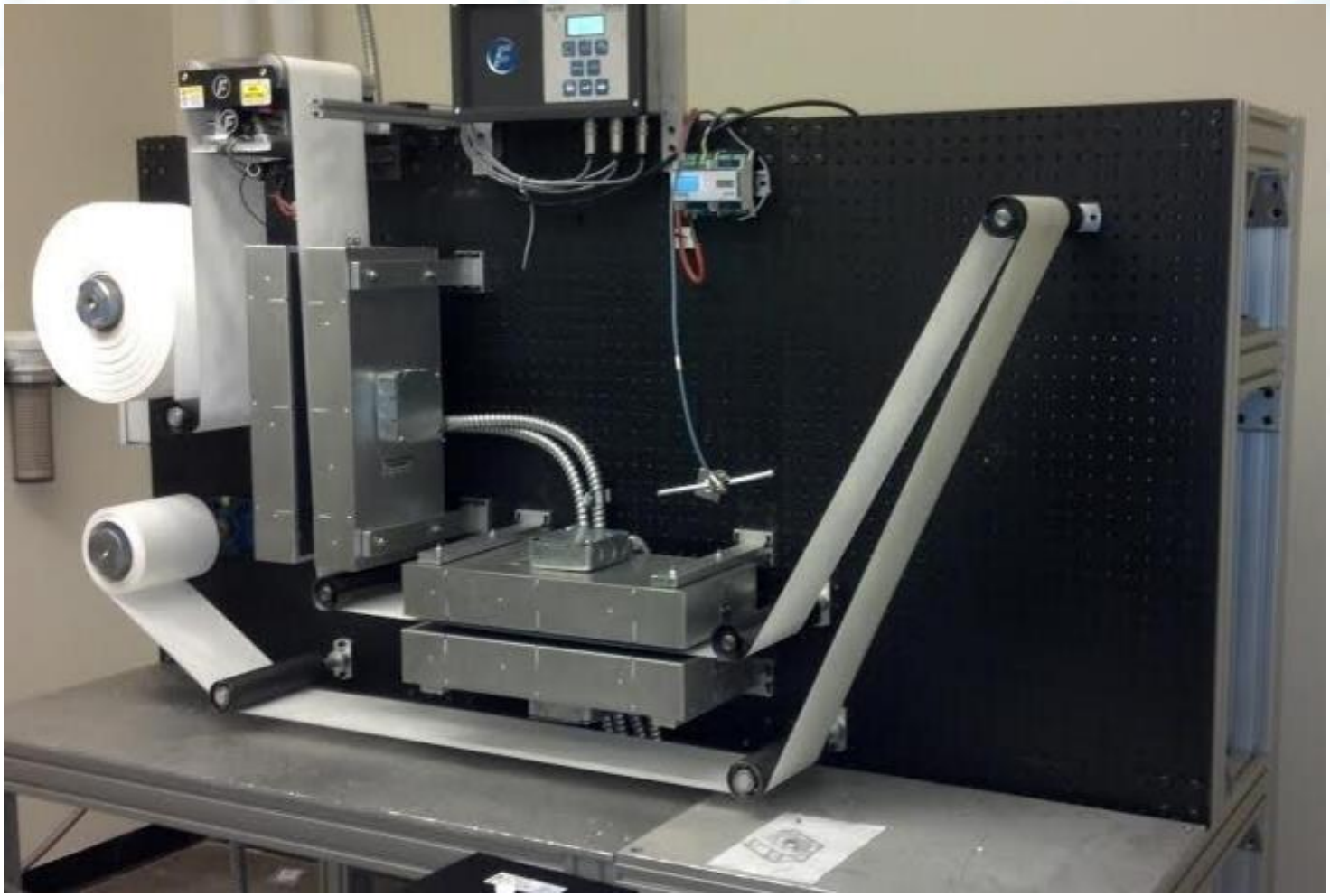
- Throughput
  - Spatial ALD = 20 cycles/min.
  - mLbL = 0.5 cycle/min.
- Comparable growth rate



In collaboration with S. George and D. Higgs, UC Boulder.

MEMBRANE INNOVATION – R2R OPPORTUNITIES

FUNCTIONAL POLYMERS



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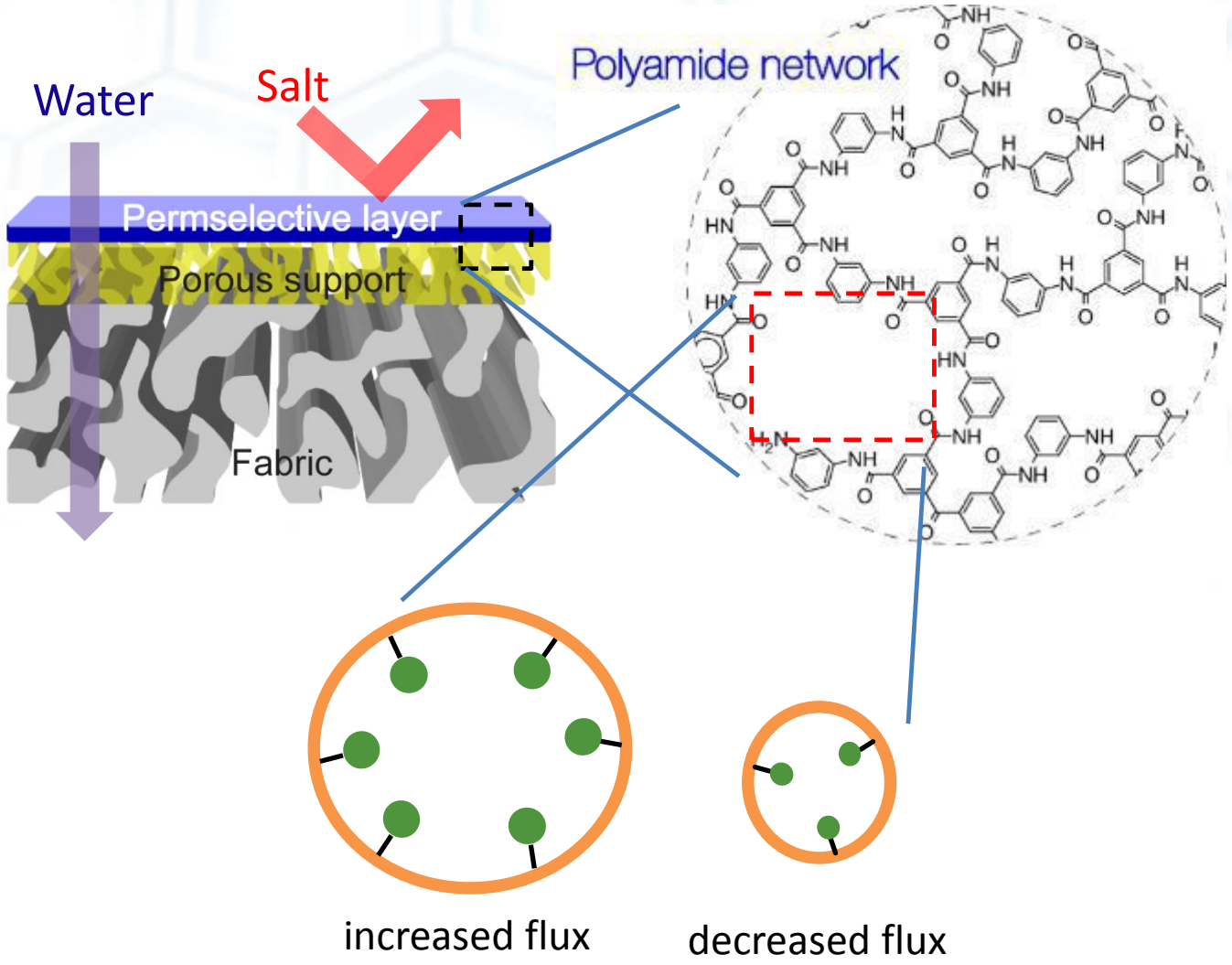
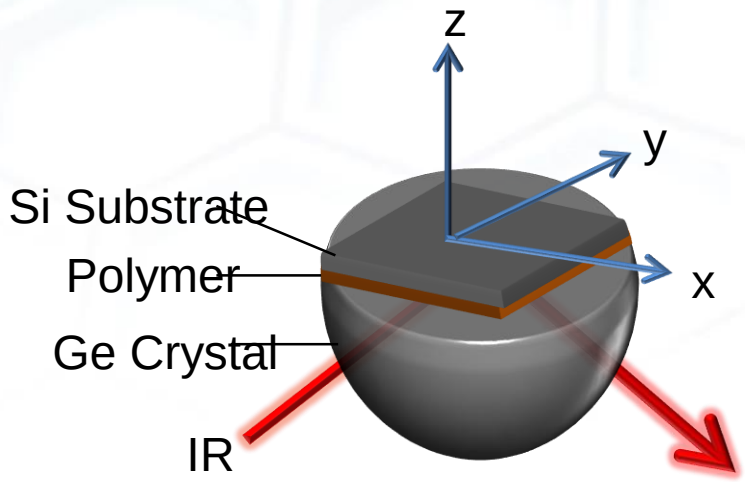
- Current (TFC) innovations
- Measurement innovations
- Opportunities

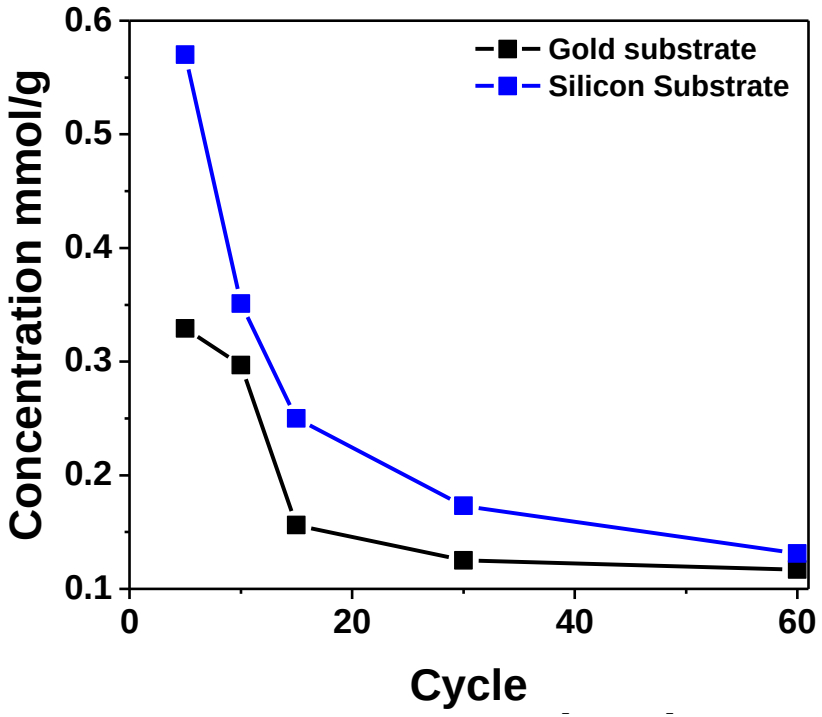
THIN FILM COMPOSITE MEMBRANES (TFC)



MEASUREMENT INNOVATION – CHEMICAL ANALYSIS

Traditional vibrational spectroscopy is not sensitive enough to measure extremely thin membranes

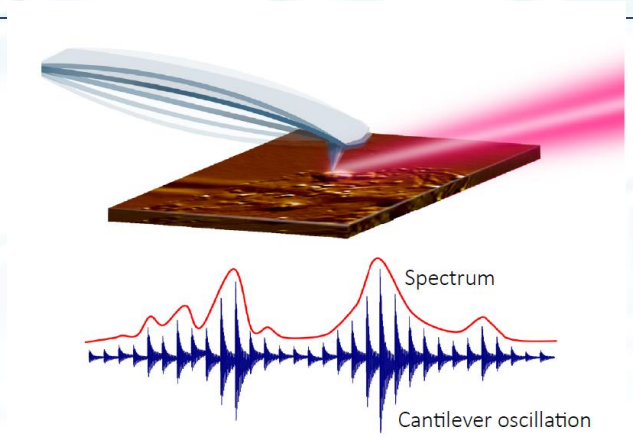


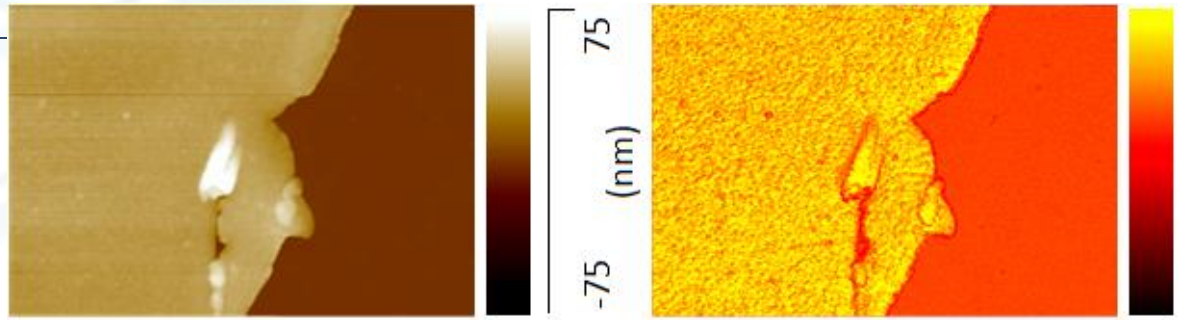


- There is thought to be a correlation between free acid and water flux
- We now have a measurement tool to track free acid content as we change variables in the system

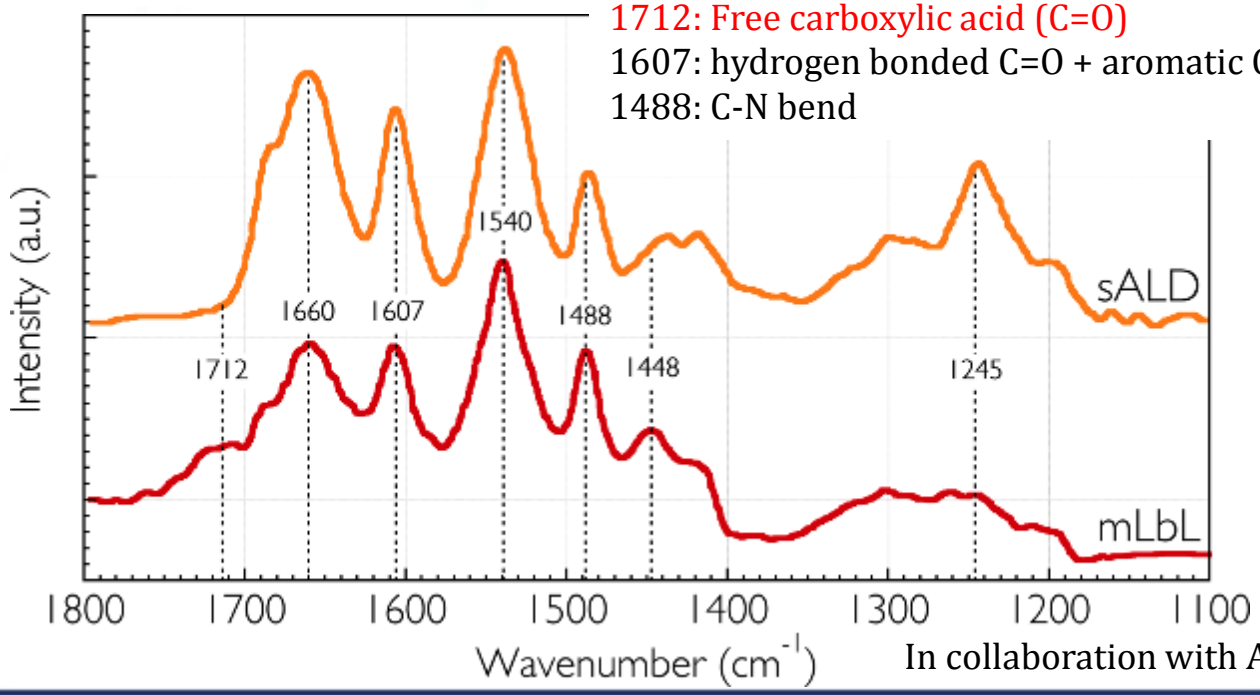
In collaboration with TJ Zimudzi and M. Hickner, Penn State.

MEASUREMENT INNOVATION – CHEMICAL ANALYSIS





1660, 1540: Amide I,II
1200-1370: Amide III, C-N stretch from Amine
1712: Free carboxylic acid (C=O)
1607: hydrogen bonded C=O + aromatic C-C stretch
1488: C-N bend



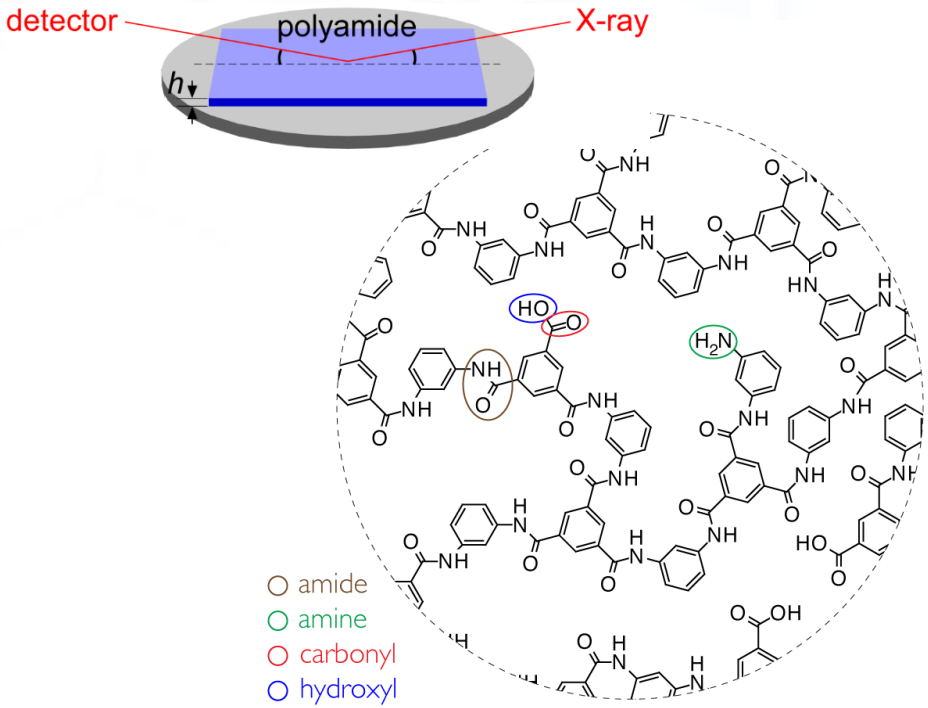
In collaboration with Anasys Instruments.

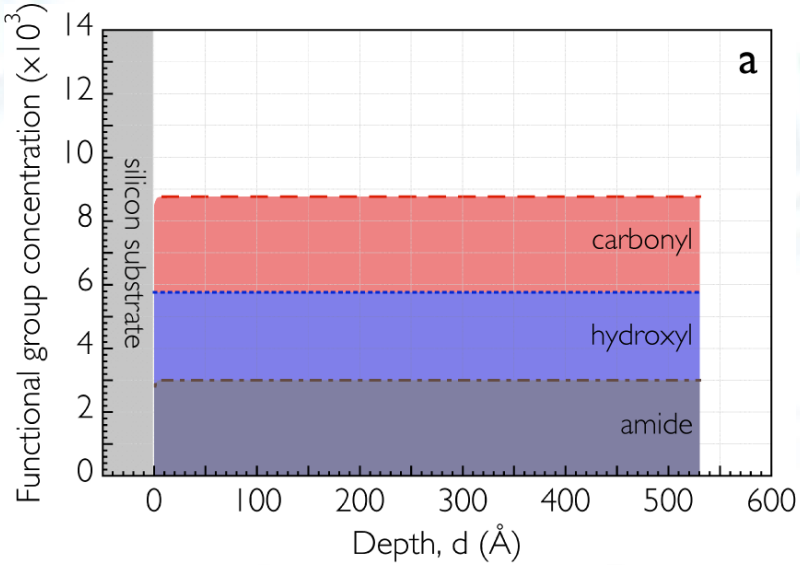
MEASUREMENT INNOVATION – CHEMICAL ANALYSIS

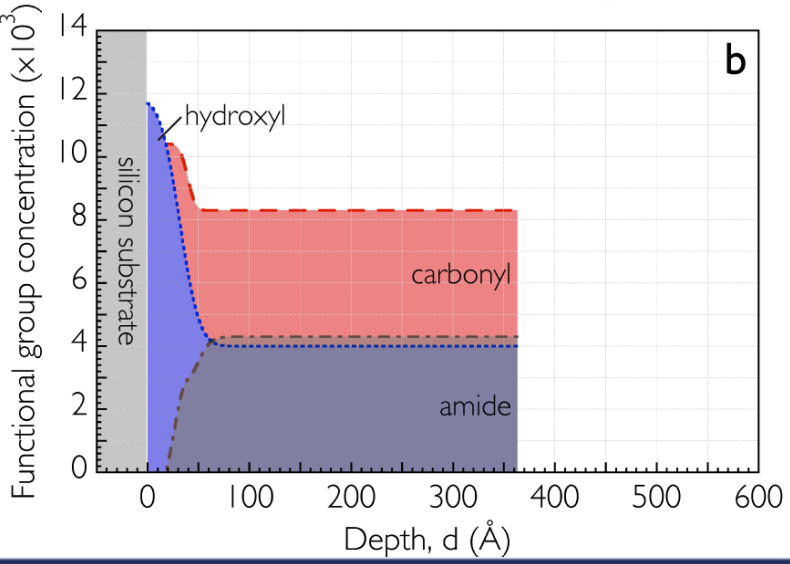
FUNCTIONAL POLYMERS

Resonant soft x-ray reflectivity (RSoXR)

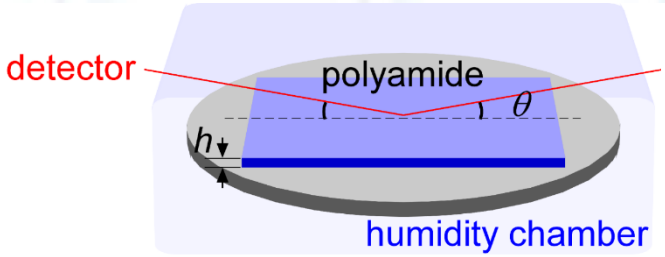
Near an atomic absorption edge, the refractive index profile will change based on the functional group, distance from the edge and functional group density.



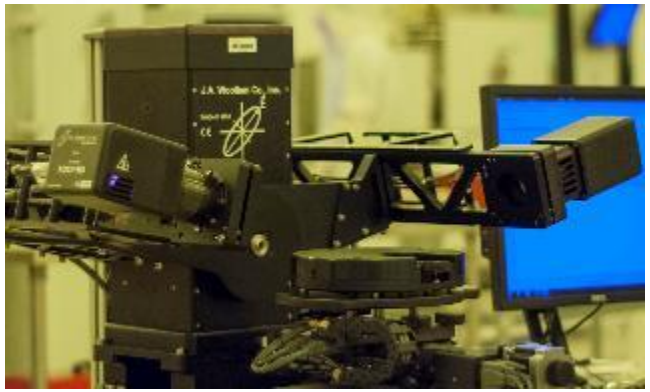




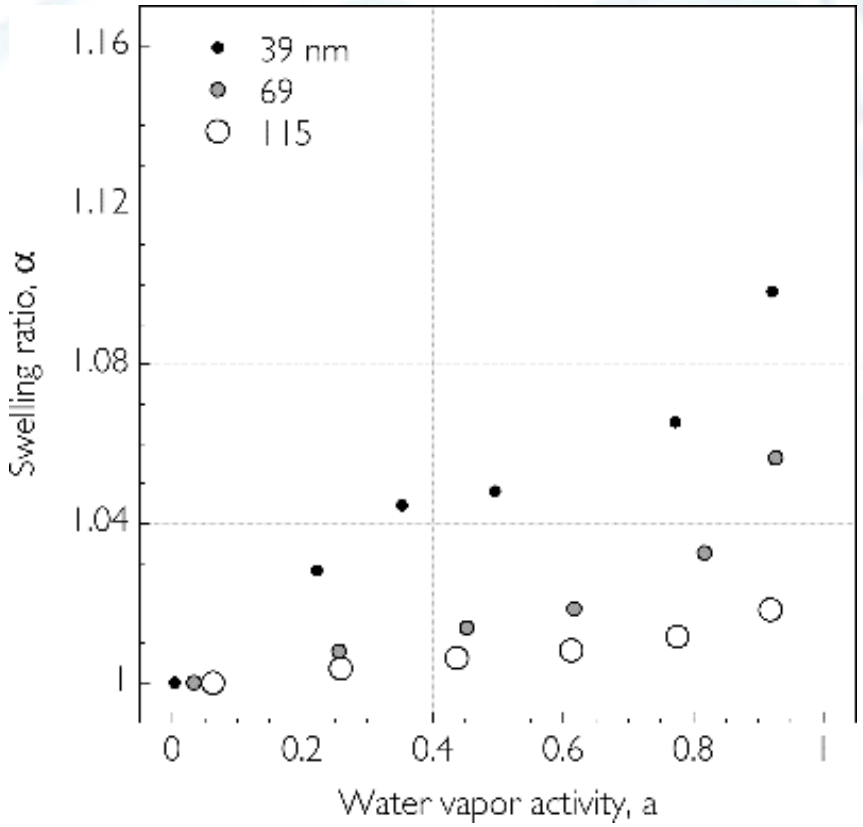
MEASUREMENT INNOVATION – SWELLING



ellipsometer



in-situ
liquid cell

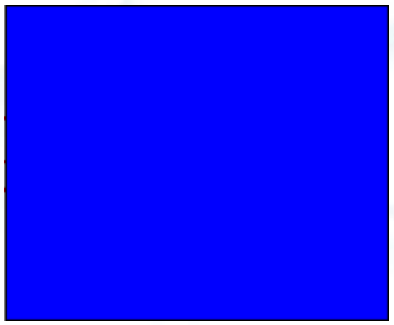


- Swelling behavior is a measure of the water content within the film
- Can correlate water content with free acid content in the membrane

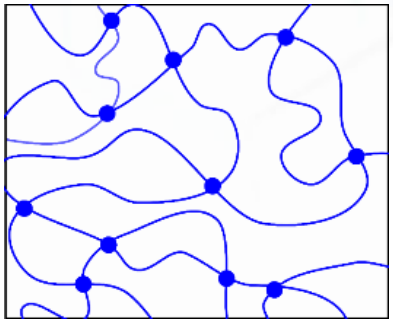
MEASUREMENT INNOVATION – DYNAMICS

FUNCTIONAL POLYMERS

- Probes molecular motions
- Influence of polymer dynamics

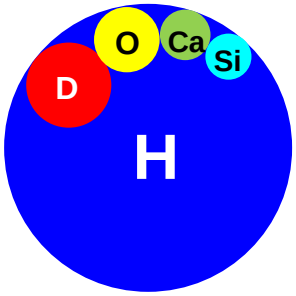


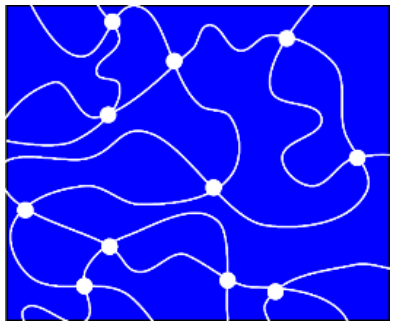
hydrated w/ H_2O



hydrated w/ D_2O

contrast

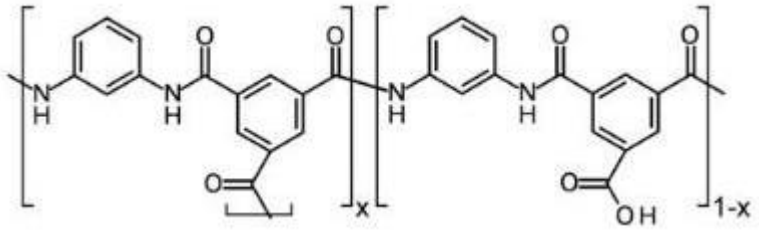




H_2O – D_2O

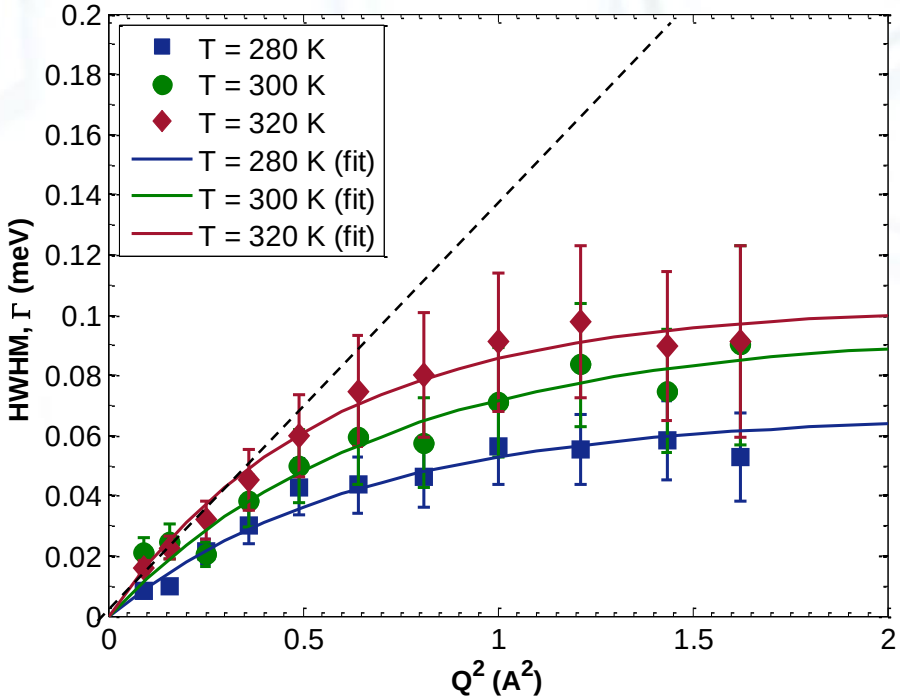
MEASUREMENT INNOVATION – TRANSPORT (WATER)

FUNCTIONAL POLYMERS



Fickian Diffusion:

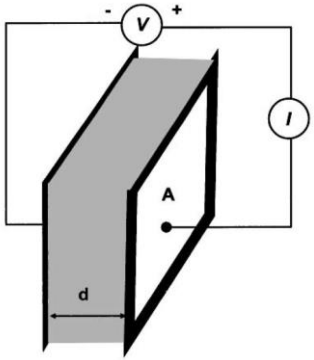
$\Gamma \propto Q^2$



- Fraction of non-mobile species (bound water)
- Effective cage size where water rattles around
- Residence time of water in that cage

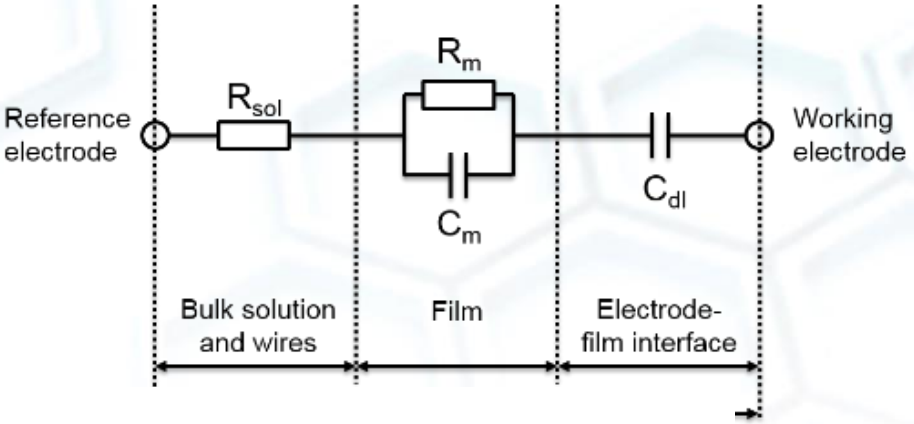
MEASUREMENT INNOVATION – TRANSPORT (SALT)

Electrochemical Impedance Spectroscopy
Traditionally a tool for electrochemists/metallurgists

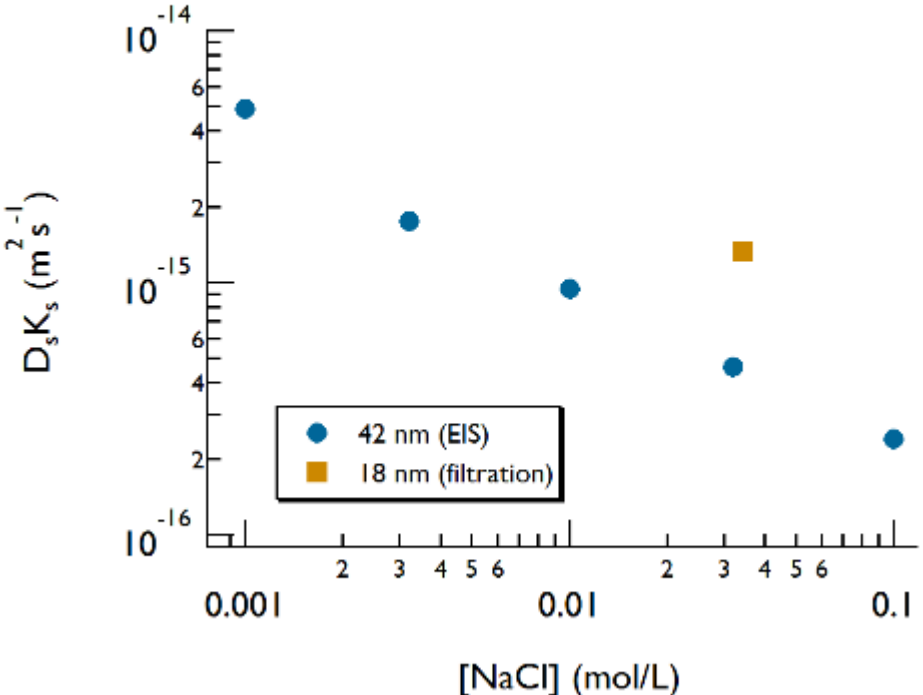


$$C_m = \frac{A}{\delta}\varepsilon\varepsilon_0$$

$$R_m = \frac{\delta}{A}\frac{RT}{F^2}\frac{1}{\sum D_i K_i c_i}$$



Intrinsic permeability

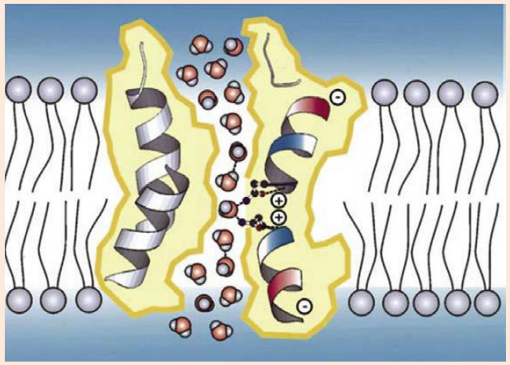


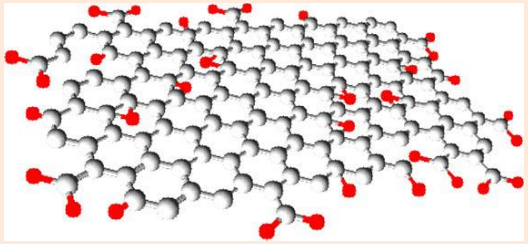
OVERVIEW

- Thin film composite (TFC) membranes
- Current (TFC) innovations
- Measurement innovations
- Opportunities

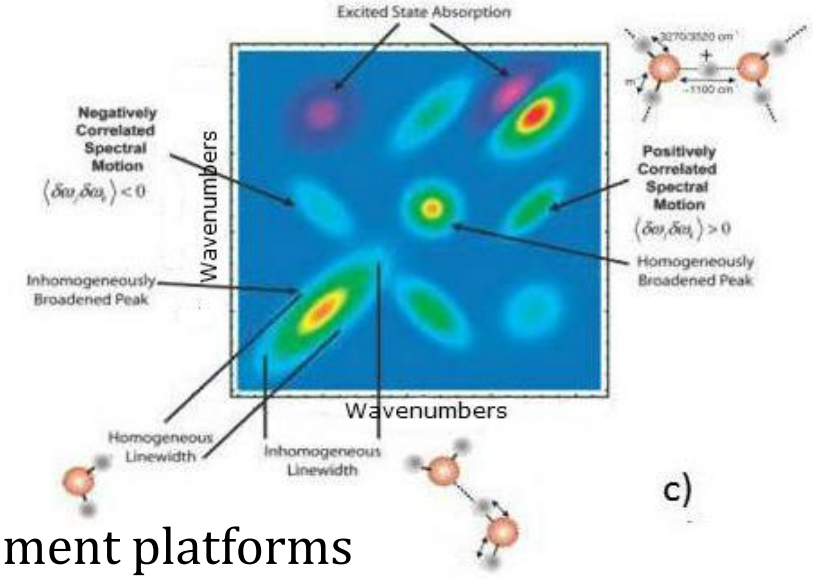
OPPORTUNITIES

New membranes, nanomaterials

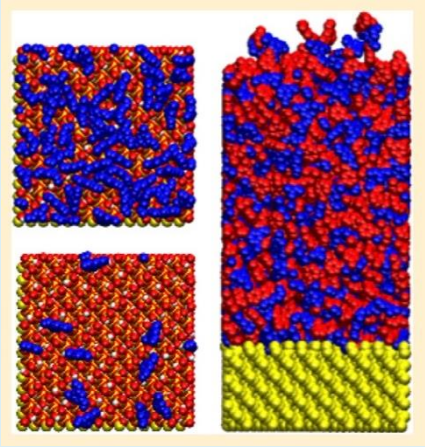


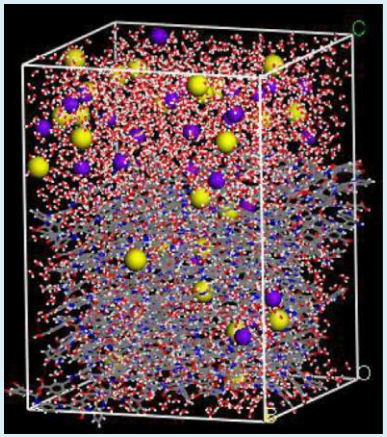


New measurement platforms



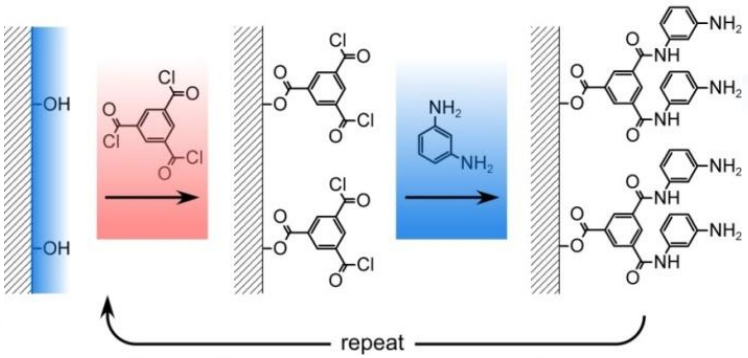
Modeling





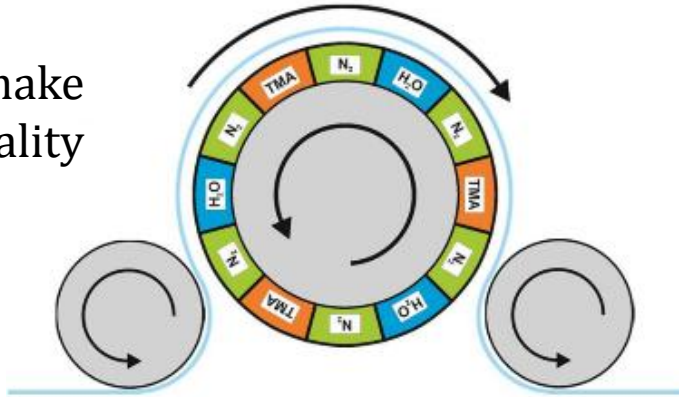
CONCLUDING THOUGHTS

- Water and water purification is critical to economic and national security
- Immense opportunities for the polymer science and beyond



- Membrane innovations go hand-in-hand with innovations in measurement science (structure/property)

- Scalable manufacturing is needed to make these new membranes a reality



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